

\$%^STN;HighlightOn= \*\*\*;HighlightOff=\*\*\* ;

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LOGINID:SSPTABAM1797

PASSWORD:

TERMINAL (ENTER 1, 2, 3, OR ?):2

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NEWS 2 AUG 10 Time limit for inactive STN sessions doubles to 40  
minutes  
NEWS 3 AUG 18 COMPENDEX indexing changed for the Corporate Source  
(CS) field  
NEWS 4 AUG 24 ENCOMPLIT/ENCOMPLIT2 reloaded and enhanced  
NEWS 5 AUG 24 CA/CAPLUS enhanced with legal status information for  
U.S. patents  
NEWS 6 SEP 09 50 Millionth Unique Chemical Substance Recorded in  
CAS REGISTRY  
NEWS 7 SEP 11 WPIDS, WPINDEX, and WPIX now include Japanese FTERM  
thesaurus  
NEWS 8 OCT 21 Derwent World Patents Index Coverage of Indian and  
Taiwanese Content Expanded  
NEWS 9 OCT 21 Derwent World Patents Index enhanced with human  
translated claims for Chinese Applications and  
Utility Models  
NEWS 10 NOV 23 Addition of SCAN format to selected STN databases  
NEWS 11 NOV 23 Annual Reload of IFI Databases  
NEWS 12 DEC 01 FRFULL Content and Search Enhancements  
NEWS 13 DEC 01 DGENE, USGENE, and PCTGEN: new percent identity  
feature for sorting BLAST answer sets  
NEWS 14 DEC 02 Derwent World Patent Index: Japanese FI-TERM  
thesaurus added  
NEWS 15 DEC 02 PCTGEN enhanced with patent family and legal status  
display data from INPADOCDB  
NEWS 16 DEC 02 USGENE: Enhanced coverage of bibliographic and  
sequence information

NEWS EXPRESS MAY 26 09 CURRENT WINDOWS VERSION IS V8.4,  
AND CURRENT DISCOVER FILE IS DATED 06 APRIL 2009.

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FILE 'HOME' ENTERED AT 12:17:04 ON 05 DEC 2009

=>

=> file registry

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.22

0.22

FILE 'REGISTRY' ENTERED AT 12:17:20 ON 05 DEC 2009

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DICTIONARY FILE UPDATES: 4 DEC 2009 HIGHEST RN 1196030-76-8

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<http://www.cas.org/support/stngen/stdoc/properties.html>

=> s 110-98-5/rn

L1 1 110-98-5/RN

=> d L1

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN

RN \*\*\*110-98-5\*\*\* REGISTRY

ED Entered STN: 16 Nov 1984

CN 2-Propanol, 1,1'-oxybis- (CA INDEX NAME)

OTHER CA INDEX NAMES:

CN 2-Propanol, 1,1'-oxydi- (6CI, 7CI, 8CI)

OTHER NAMES:

CN 1,1'-Dimethyldiethylene glycol

CN 1,1'-Oxydi-2-propanol

CN Bis(2-hydroxypropyl) ether

CN NSC 8688

MF C6 H14 O3

CI COM

LC STN Files: ANABSTR, AQUIRE, BEILSTEIN\*, CA, CAPLUS, CASREACT,

CHEMCATS,

CHEMLIST, CSCHEM, HSDB\*, IFICDB, IFIPAT, IFIUDB, MSDS-OHS,

RTECS\*,

SPECINFO, TOXCENTER, ULIDAT, USPAT2, USPATFULL, USPATOLD

(\*File contains numerically searchable property data)  
Other Sources: DSL\*\*, EINECS\*\*, TSCA\*\*  
(\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 1 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

134 REFERENCES IN FILE CA (1907 TO DATE)  
4 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
135 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 25265-71-8/rn

L2 1 25265-71-8/RN

=> d L2

L2 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN  
RN \*\*\*25265-71-8\*\*\* REGISTRY  
ED Entered STN: 16 Nov 1984  
CN Propanol, oxybis- (CA INDEX NAME)  
OTHER CA INDEX NAMES:  
CN Dipropylene glycol (6CI)  
OTHER NAMES:  
CN ADK DPG-RF  
DR 25322-23-0, 75047-14-2, 78644-49-2, 27941-90-8, 27941-91-9, 28678-  
26-4,  
30370-61-7  
MF C6 H14 O3  
CI IDS, COM  
LC STN Files: AGRICOLA, ANABSTR, AQUIRE, BIOSIS, BIOTECHNO, CA,  
CAPLUS,  
CASREACT, CBNB, CHEMCATS, CHEMLIST, CHEMSAFE, CIN, CSCHEM, CSNB,  
DETERM\*, EMBASE, HSDB\*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MSDS-  
OHS,  
PIRA, PROMT, RTECS\*, TOXCENTER, TULSA, ULIDAT, USPAT2, USPATFULL,  
USPATOLD  
(\*File contains numerically searchable property data)  
Other Sources: DSL\*\*, EINECS\*\*, TSCA\*\*  
(\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 2 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

4812 REFERENCES IN FILE CA (1907 TO DATE)  
684 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
4820 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 7320-37-8/rn

L3 1 7320-37-8/RN

=> d L3

```

L3  ANSWER 1 OF 1  REGISTRY  COPYRIGHT 2009 ACS on STN
RN  ***7320-37-8***      REGISTRY
ED  Entered STN:  16 Nov 1984
CN  Oxirane, 2-tetradecyl- (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN  Hexadecane, 1,2-epoxy- (6CI, 7CI, 8CI)
CN  Oxirane, tetradecyl- (9CI)
OTHER NAMES:
CN  1,2-Epoxyhexadecane
CN  1,2-Epoxyhexadecene
CN  1,2-Hexadecene epoxide
CN  1,2-Hexadecylene oxide
CN  1-Hexadecene oxide
CN  Cyracure UVR 6216
CN  Hexadecylene oxide
CN  Tetradecyloxirane
CN  UVR 6216
CN  Vikolox 16
DR  151284-10-5
MF  C16 H32 O
CI  COM
LC  STN Files:  ANABSTR, BEILSTEIN*, BIOSIS, CA, CAPLUS, CASREACT,
CHEMCATS,
      CHEMINFORMRX, CHEMLIST, CSCHEM, CSNB, HSDB*, IFICDB, IFIPAT,
IFIUDB,
      PIRA, PROMT, RTECS*, SPECINFO, TOXCENTER, USPAT2, USPATFULL,
USPATOLD
      (*File contains numerically searchable property data)
      Other Sources:  EINECS**, NDSL**, TSCA**
      (**Enter CHEMLIST File for up-to-date regulatory information)

```

/ Structure 3 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

```

      345 REFERENCES IN FILE CA (1907 TO DATE)
      105 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
      345 REFERENCES IN FILE CAPLUS (1907 TO DATE)

```

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=> s 280-57-9/rn
L4      1 280-57-9/RN

```

=> d L4

```

L4  ANSWER 1 OF 1  REGISTRY  COPYRIGHT 2009 ACS on STN
RN  ***280-57-9***      REGISTRY
ED  Entered STN:  16 Nov 1984
CN  1,4-Diazabicyclo[2.2.2]octane (CA INDEX NAME)
OTHER NAMES:
CN  1,4-Ethylenepiperazine
CN  33LV
CN  A 33
CN  Activator 105E
CN  AE 33
CN  Bicyclo[2.2.2]-1,4-diazaoctane

```

CN D 33LV  
 CN Dabco  
 CN Dabco 33LV  
 CN Dabco 3LV  
 CN DABCO Crystal  
 CN Dabco Crystalline  
 CN Dabco L 1202  
 CN Dabco S 25  
 CN Jeffcat TD 100  
 CN Kaolizer 31  
 CN L 33  
 CN L 33E  
 CN LC 96003  
 CN LV 33  
 CN Minico L 1020  
 CN N,N'-endo-Ethylenepiperazine  
 CN Niaux A 33  
 CN NSC 56362  
 CN PC CAT TD 33  
 CN PC-TD  
 CN Polycat 33LV  
 CN TD 100  
 CN TED  
 CN TEDA  
 CN Teda L 33  
 CN Tegamine 33  
 CN Tego Amine  
 CN Tegoamin 33  
 CN Texacat TD 100  
 CN Texacat TD 33  
 CN Thancat TD 33  
 CN Thancat TD 33A  
 CN Toral SM 2  
 CN Toyocat L 33  
 CN Toyocat TEDA L 33  
 CN Triethylenediamine  
 DR 746642-46-6, 903524-95-8, 165724-47-0, 23790-33-2, 101484-19-9,  
 150605-01-9, 88935-43-7, 203072-11-1, 309955-09-7  
 MF C6 H12 N2  
 CI COM, RPS  
 LC STN Files: AGRICOLA, ANABSTR, AQUIRE, BEILSTEIN\*, BIOSIS,  
 BIOTECHNO, CA,  
 CAPLUS, CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN,  
 CSCHEM,  
 CSNB, DETHERM\*, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT,  
 ENCOMPPAT2,  
 GMELIN\*, HSDB\*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MRCK\*, MSDS-OHS,  
 PIRA,  
 PROMT, RTECS\*, SPECINFO, SYNTHLINE, TOXCENTER, ULIDAT, USPAT2,  
 USPATFULL, USPATOLD  
 (\*File contains numerically searchable property data)  
 Other Sources: DSL\*\*, EINECS\*\*, TSCA\*\*  
 (\*\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 4 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

6696 REFERENCES IN FILE CA (1907 TO DATE)  
 321 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
 6716 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> file caplus uspatfull  
 COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
33.64	33.86

FULL ESTIMATED COST

FILE 'CAPLUS' ENTERED AT 12:49:23 ON 05 DEC 2009  
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=> s L4 and L3 and L2  
 L5 1 L4 AND L3 AND L2

=> d L5 ibib hit

L5 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2009 ACS on STN  
 ACCESSION NUMBER: 2005:1027004 CAPLUS <<LOGINID::20091205>>  
 DOCUMENT NUMBER: 143:328922  
 TITLE: Hydrocarbon desulfurization with mercaptan  
 removal by treatment with alicyclic tertiary amines and  
 nucleophilic acceptors  
 INVENTOR(S): Schield, John A.; Cappel, Weldon John  
 PATENT ASSIGNEE(S): Baker Hughes Incorporated, USA  
 SOURCE: PCT Int. Appl., 23 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	----	-----	-----	-----
WO 2005087899	A1	20050922	WO 2004-US4011	
20040211				
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA,			
CH,	CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB,			
GD,	GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ,			
LC,	LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA,			
NI,	NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL,			
SY,	TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,			
ZW				
RW:	BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM,			
AZ,	BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,			
EE,				

ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI,  
 SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,  
 TD, TG CA 2554548 A1 20050922 CA 2004-2554548  
 20040211 EP 1713885 A1 20061025 EP 2004-710238  
 20040211 R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC,  
 PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, SK  
 US 20070142244 A1 20070621 US 2006-588341  
 20060803  
 PRIORITY APPLN. INFO.: WO 2004-US4011 W  
 20040211  
 ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT  
 OTHER SOURCE(S): MARPAT 143:328922  
 REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE  
 FOR THIS

RECORD. ALL CITATIONS AVAILABLE IN THE RE

FORMAT  
 IT \*\*\*280-57-9\*\*\* , 1,4-Diazabicyclo[2.2.2]octane 3001-72-7,  
 1,5-Diazabicyclo[4.3.0]non-5-ene 6674-22-2,  
 1,8-Diazabicyclo[5.4.0]undec-7-ene  
 RL: CPS (Chemical process); PEP (Physical, engineering or chemical  
 process); PROC (Process)  
 (hydrocarbon desulfurization with mercaptan removal by treatment  
 with alicyclic tertiary amines and nucleophilic acceptors)  
 IT \*\*\*25265-71-8\*\*\* , Dipropylene glycol  
 RL: NUU (Other use, unclassified); USES (Uses)  
 (hydrocarbon desulfurization with mercaptan removal by treatment  
 with alicyclic tertiary amines and nucleophilic acceptors)  
 IT 463-73-0D, Chloroformic acid, compds. 2817-45-0D, Phosphoramidic  
 acid,  
 compds. \*\*\*7320-37-8\*\*\* , 1,2-Epoxyhexadecane 19270-07-6D,  
 Cyanoformic acid, compds.  
 RL: CPS (Chemical process); PEP (Physical, engineering or chemical  
 process); PROC (Process)  
 (nucleophilic acceptors; hydrocarbon desulfurization with  
 mercaptan removal by treatment with alicyclic tertiary amines and  
 nucleophilic acceptors)

=> s L4 and L2  
 L6 84 L4 AND L2  
  
 => s L6 and epoxide  
 L7 11 L6 AND EPOXIDE  
  
 => d L7 ti

L7 ANSWER 1 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN  
 TI Hydrocarbon desulfurization with mercaptan removal by treatment  
 with alicyclic tertiary amines and nucleophilic acceptors

=> d L7 1-11 ti

L7 ANSWER 1 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN  
TI Hydrocarbon desulfurization with mercaptan removal by treatment  
with  
alicyclic tertiary amines and nucleophilic acceptors

L7 ANSWER 2 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN  
TI Flame retardant, additive compositions, and flame retardant  
polyurethanes

L7 ANSWER 3 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN  
TI Molding of polyisocyanurate heat-resistant resins

L7 ANSWER 4 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN  
TI Curable epoxy resin containing molding compositions

L7 ANSWER 5 OF 11 USPATFULL on STN  
TI System, method and composition for adhering preformed  
thermoplastic  
traffic control signage to pavement

L7 ANSWER 6 OF 11 USPATFULL on STN  
TI Method of producing flexible laminates

L7 ANSWER 7 OF 11 USPATFULL on STN  
TI SELF-PHOTOINITIATING MULTIFUNCTIONAL URETHANE OLIGOMERS  
CONTAINING  
PENDANT ACRYLATE GROUPS

L7 ANSWER 8 OF 11 USPATFULL on STN  
TI Flame retardant, additive compositions, and flame retardant  
polyurethanes

L7 ANSWER 9 OF 11 USPATFULL on STN  
TI Silicon and phosphorus containing compositions

L7 ANSWER 10 OF 11 USPATFULL on STN  
TI Curable epoxy resin containing molding compositions

L7 ANSWER 11 OF 11 USPATFULL on STN  
TI Polyepoxide curing by polymercaptans catalyzed by dimethylamino  
alkyl  
ethers

=>

=>

---Logging off of STN---

=>

Executing the logoff script...

=> LOG Y



COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

65.15

99.01

STN INTERNATIONAL LOGOFF AT 13:28:22 ON 05 DEC 2009

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PASSWORD:

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thesaurus  
NEWS 8 OCT 21 Derwent World Patents Index Coverage of Indian and  
Taiwanese Content Expanded  
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feature for sorting BLAST answer sets  
NEWS 14 DEC 02 Derwent World Patent Index: Japanese FI-TERM  
thesaurus added  
NEWS 15 DEC 02 PCTGEN enhanced with patent family and legal status  
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NEWS 16 DEC 02 USGENE: Enhanced coverage of bibliographic and  
sequence information

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AND CURRENT DISCOVER FILE IS DATED 06 APRIL 2009.

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\* \* \* \* \* STN Columbus \* \* \* \* \*

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=> file registry		
COST IN U.S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	0.22	0.22

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DICTIONARY FILE UPDATES: 4 DEC 2009 HIGHEST RN 1196030-76-8

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<http://www.cas.org/support/stngen/stdnec/properties.html>

=> s 6674-22-2/rn  
L1 1 6674-22-2/RN

=> d L1

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN  
RN \*\*\*6674-22-2\*\*\* REGISTRY  
ED Entered STN: 16 Nov 1984  
CN Pyrimido[1,2-a]azepine, 2,3,4,6,7,8,9,10-octahydro- (CA INDEX NAME)  
OTHER NAMES:  
CN 1,8-Diaza-7-bicyclo[5.4.0]undecene  
CN 1,8-Diazabicyclo[5.4.0]undec-7-ene  
CN 1,8-Diazabicyclo[5.4.0]undecene-7  
CN 2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-a]azepine  
CN Alcanpoudre DBU 70-3KG  
CN Amicure DBUE  
CN Dabco DBU

CN DBU  
CN NSC 111184  
CN NSC 230466  
CN Polycat DBU  
CN U-CAT SA 851  
DR 51301-56-5, 69722-76-5, 78995-63-8, 83329-50-4, 31171-04-7, 41015-70-7  
MF C9 H16 N2  
CI COM  
LC STN Files: ANABSTR, BEILSTEIN\*, BIOSIS, CA, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, GMELIN\*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MSDS-OHS, SPECINFO, TOXCENTER, USPAT2, USPATFULL, USPATOLD  
(\*File contains numerically searchable property data)  
Other Sources: DSL\*\*, EINECS\*\*, TSCA\*\*  
(\*\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 5 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

4005 REFERENCES IN FILE CA (1907 TO DATE)  
152 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
4035 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 3001-72-7/rn  
L2 1 3001-72-7/RN

=> d L2

L2 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN  
RN \*\*\*3001-72-7\*\*\* REGISTRY  
ED Entered STN: 16 Nov 1984  
CN Pyrrolo[1,2-a]pyrimidine, 2,3,4,6,7,8-hexahydro- (CA INDEX NAME)  
OTHER NAMES:  
CN 1,5-Diazabicyclo[4.3.0]non-5-ene  
CN 1,5-Diazabicyclo[4.3.0]nonene-5  
CN 1,5-Diazobicyclo[4.3.0]non-5-ene  
CN 2,3,4,6,7,8-Hexahydropyrrolo[1,2-a]pyrimidine  
CN DBN  
CN DBN (heterocycle)  
CN NBU  
CN NSC 118106  
DR 25986-32-7, 312727-86-9  
MF C7 H12 N2  
CI COM  
LC STN Files: ANABSTR, BEILSTEIN\*, BIOSIS, CA, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CHEMLIST, CSCHEM, GMELIN\*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MSDS-OHS, SPECINFO, SYNTHLINE, TOXCENTER, USPAT2, USPATFULL, USPATOLD  
(\*File contains numerically searchable property data)

Other Sources: EINECS\*\*  
(\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 6 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

1103 REFERENCES IN FILE CA (1907 TO DATE)  
44 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
1110 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 280-57-9/rn  
L3 1 280-57-9/RN

=>

=> file caplus uspatfull  
COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
17.54	17.76

FULL ESTIMATED COST

FILE 'CAPLUS' ENTERED AT 14:11:39 ON 05 DEC 2009  
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FILE 'USPATFULL' ENTERED AT 14:11:39 ON 05 DEC 2009  
CA INDEXING COPYRIGHT (C) 2009 AMERICAN CHEMICAL SOCIETY (ACS)

=> s L1 OR L2 OR L3  
L4 12836 L1 OR L2 OR L3

=> s L4 and epoxide  
L5 515 L4 AND EPOXIDE

=> s L5 AND (thiol OR mercaptan OR desulfurization)  
L6 102 L5 AND (THIOL OR MERCAPTAN OR DESULFURIZATION)

=> s L6 AND (isopropanol OR butanediol OR (tetramethylene (w) glycol) OR  
(dipropylene adj glycol))  
L7 60 L6 AND (ISOPROPANOL OR BUTANEDIOL OR (TETRAMETHYLENE (W)  
GLYCOL  
) OR (DIPROPYLENE ADJ GLYCOL))

=> d L7 1-60 ti

L7 ANSWER 1 OF 60 USPATFULL on STN  
TI CEMENT PRODUCTS AND METHODS OF MAKING AND USING THE SAME

L7 ANSWER 2 OF 60 USPATFULL on STN  
TI Bioabsorbable Surgical Composition

L7 ANSWER 3 OF 60 USPATFULL on STN  
TI Methods and Systems for Making \*\*\*Thiol\*\*\* Compounds from  
Terminal  
Olefinic Compounds

L7 ANSWER 4 OF 60 USPATFULL on STN

TI CURABLE COMPOSITIONS BASED ON POLYURETIDIONES, POLYTHIOLS AND  
 PHOTOACTIVABLE BASES AND GENERATION OF ISOCYANATES FROM  
 URETIDIONES

L7 ANSWER 5 OF 60 USPATFULL on STN  
 TI Liquid fluorine-containing and two-component compositions for the  
 surface treatment of mineral and non-mineral substrates

L7 ANSWER 6 OF 60 USPATFULL on STN  
 TI ANTI-MICROBIAL AGENTS AND USES THEREOF

L7 ANSWER 7 OF 60 USPATFULL on STN  
 TI Methods and compounds for curing polythiourethane compositions

L7 ANSWER 8 OF 60 USPATFULL on STN  
 TI Methods and systems for the selective formation of thiourethane  
 bonds  
 and compounds formed therefrom

L7 ANSWER 9 OF 60 USPATFULL on STN  
 TI ORGANOMETALLIC COMPOSITIONS AND COATING COMPOSITIONS

L7 ANSWER 10 OF 60 USPATFULL on STN  
 TI Thiourethane Compositions and Processes for Making and Using Same

L7 ANSWER 11 OF 60 USPATFULL on STN  
 TI Method of producing flexible laminates

L7 ANSWER 12 OF 60 USPATFULL on STN  
 TI Hardener for Epoxy Resin and Epoxy Resin Composition

L7 ANSWER 13 OF 60 USPATFULL on STN  
 TI MICROBIAL TRANSFORMATION METHOD FOR THE PREPARATION OF AN  
 EPOTHILONE

L7 ANSWER 14 OF 60 USPATFULL on STN  
 TI \*\*\*MERCAPTAN\*\*\* -HARDENED EPOXY POLYMER COMPOSITIONS AND  
 PROCESSES  
 FOR MAKING AND USING SAME

L7 ANSWER 15 OF 60 USPATFULL on STN  
 TI POLYMER COMPOSITIONS AND PROCESSES FOR MAKING AND USING SAME

L7 ANSWER 16 OF 60 USPATFULL on STN  
 TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon  
 bonds

L7 ANSWER 17 OF 60 USPATFULL on STN  
 TI ORGANOMETALLIC COMPOSITIONS AND COATING COMPOSITIONS

L7 ANSWER 18 OF 60 USPATFULL on STN  
 TI Pyrrolotriazine inhibitors of kinases

L7 ANSWER 19 OF 60 USPATFULL on STN  
 TI Polythiourethane compositions and processes for making and using  
 same

L7 ANSWER 20 OF 60 USPATFULL on STN  
 TI Retroviral protease inhibitors

L7 ANSWER 21 OF 60 USPATFULL on STN  
TI Retroviral protease inhibitors

L7 ANSWER 22 OF 60 USPATFULL on STN  
TI \*\*\*Thiol\*\*\* ester compositions and processes for making and  
using same

L7 ANSWER 23 OF 60 USPATFULL on STN  
TI Organometallic compositions and coating compositions

L7 ANSWER 24 OF 60 USPATFULL on STN  
TI Pyrrolotriazine inhibitors of kinases

L7 ANSWER 25 OF 60 USPATFULL on STN  
TI Controlled release fertilizer material and process for production  
thereof

L7 ANSWER 26 OF 60 USPATFULL on STN  
TI Pyrrolotriazine inhibitors of kinases

L7 ANSWER 27 OF 60 USPATFULL on STN  
TI Radiation-curable coatings for plastic substrates from  
multifunctional acrylate oligomers

L7 ANSWER 28 OF 60 USPATFULL on STN  
TI Copper-catalyzed formation of carbon heteroatom and carbon-carbon  
bonds

L7 ANSWER 29 OF 60 USPATFULL on STN  
TI Anionic and Lewis base photopolymerization process and its use  
for making optical articles

L7 ANSWER 30 OF 60 USPATFULL on STN  
TI \*\*\*Thiol\*\*\* ester compositions and processes for making and  
using same

L7 ANSWER 31 OF 60 USPATFULL on STN  
TI \*\*\*Thiol\*\*\* ester compositions and processes for making and  
using same

L7 ANSWER 32 OF 60 USPATFULL on STN  
TI Compositions useful as coatings, their preparation, and articles  
made therefrom

L7 ANSWER 33 OF 60 USPATFULL on STN  
TI Anionic and Lewis base photopolymerization process and its use  
for making optical articles

L7 ANSWER 34 OF 60 USPATFULL on STN  
TI Photocrosslinked hydrogel blend surface coatings

L7 ANSWER 35 OF 60 USPATFULL on STN  
TI Dual cure reaction products of self-photoinitiating

multifunctional  
acrylates with \*\*\*thiols\*\*\* and synthetic methods

L7 ANSWER 36 OF 60 USPATFULL on STN  
TI Novel mono- and di-fluorinated benzothiepine compounds as  
inhibitors of  
apical sodium co-dependent bile acid transport (ASBT) and  
taurocholate  
uptake

L7 ANSWER 37 OF 60 USPATFULL on STN  
TI Microbial transformation method for the preparation of an  
epothilone

L7 ANSWER 38 OF 60 USPATFULL on STN  
TI Microbial transformation method for the preparation of an  
epothilone

L7 ANSWER 39 OF 60 USPATFULL on STN  
TI Novel mono- and di-fluorinated benzothiepine compounds as  
inhibitors of  
apical sodium co-dependent bile acid transport (ASBT) and  
taurocholate  
uptake

L7 ANSWER 40 OF 60 USPATFULL on STN  
TI Dental polymer film

L7 ANSWER 41 OF 60 USPATFULL on STN  
TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon  
bonds

L7 ANSWER 42 OF 60 USPATFULL on STN  
TI Novel benzothiepinines having activity as inhibitors of ileal bile  
acid  
transport and taurocholate uptake

L7 ANSWER 43 OF 60 USPATFULL on STN  
TI High strength epoxy adhesive and uses thereof

L7 ANSWER 44 OF 60 USPATFULL on STN  
TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon  
bonds

L7 ANSWER 45 OF 60 USPATFULL on STN  
TI Retroviral protease inhibitors

L7 ANSWER 46 OF 60 USPATFULL on STN  
TI Composition of epoxy resin, chain extender and polymeric  
toughener with  
separate base catalyst

L7 ANSWER 47 OF 60 USPATFULL on STN  
TI Substituted 5-aryl-benzothiepinines having activity as inhibitors  
of ileal  
bile acid transport and taurocholate uptake

L7 ANSWER 48 OF 60 USPATFULL on STN  
TI Primerless substrate repair with polyepoxide and polythiol

L7 ANSWER 49 OF 60 USPATFULL on STN  
 TI Reacting methylene and alkene components in presence of tertiary amine  
     reacted with \*\*\*epoxide\*\*\*

L7 ANSWER 50 OF 60 USPATFULL on STN  
 TI Isocyanate reactive blends and internal mould release composites

L7 ANSWER 51 OF 60 USPATFULL on STN  
 TI Isocyanate reactive blends and internal mould release compositions

L7 ANSWER 52 OF 60 USPATFULL on STN  
 TI Thermally curable mixture containing epoxy and formamide compounds

L7 ANSWER 53 OF 60 USPATFULL on STN  
 TI Isocyanate reactive blends and internal mould release compositions

L7 ANSWER 54 OF 60 USPATFULL on STN  
 TI Reaction product of olefinically unsaturated compounds with compounds  
     containing active hydrogen, processes for their preparation and 2-component lacquers based thereon

L7 ANSWER 55 OF 60 USPATFULL on STN  
 TI Reaction product of olefinically unsaturated compounds with compounds  
     containing active hydrogen, processes for their preparation and 2-component lacquers based thereon HOE 85/F 036J

L7 ANSWER 56 OF 60 USPATFULL on STN  
 TI Epoxy/nucleophile transesterification catalysts and thermoset coatings

L7 ANSWER 57 OF 60 USPATFULL on STN  
 TI Heat-hardenable \*\*\*epoxide\*\*\* resin mixtures

L7 ANSWER 58 OF 60 USPATFULL on STN  
 TI Process for the preparation of polyamines from N-monoaryl-N',N'-dialkyl urea compounds and their use for the synthesis of polyurethanes

L7 ANSWER 59 OF 60 USPATFULL on STN  
 TI Process for the preparation of stabilized polymer dispersions in polyol  
     at low temperature

L7 ANSWER 60 OF 60 USPATFULL on STN  
 TI Polyepoxide curing by polymercaptans catalyzed by dimethylamino alkyl ethers

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L7 ANSWER 30 OF 60 USPATFULL on STN  
 ACCESSION NUMBER: 2005:227539 USPATFULL <<LOGINID:20091205>>  
 TITLE: \*\*\*Thiol\*\*\* ester compositions and processes



for making and using same

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CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI \*\*\*Thiol\*\*\* ester compositions and processes for making and using same

AB \*\*\*Thiol\*\*\* ester compositions, methods of making the \*\*\*thiol\*\*\* ester compositions, and methods of using the \*\*\*thiol\*\*\* ester compositions are provided. In some embodiments, the \*\*\*thiol\*\*\* ester compositions include \*\*\*thiol\*\*\* esters, hydroxy \*\*\*thiol\*\*\* esters and cross-linked \*\*\*thiol\*\*\* esters. The \*\*\*thiol\*\*\* ester composition can be used to produce cross-linked \*\*\*thiol\*\*\* esters, sulfonic acid-containing esters, sulfonate containing esters and thioacrylate containing esters. The \*\*\*thiol\*\*\* ester compositions can be used to produce polythiourethanes. The polythiourethanes can be used in fertilizers and fertilizer coatings.

SUMM The invention relates to \*\*\*thiol\*\*\* containing ester compositions generally made from a reaction of unsaturated ester compositions

and a material capable of forming a \*\*\*thiol\*\*\* group. The invention also relates to the processes for preparing such \*\*\*thiol\*\*\* containing compositions and uses for the \*\*\*thiol\*\*\* containing compositions.

SUMM The present invention advantageously provides \*\*\*thiol\*\*\* containing compositions and methods of making such compositions. In addition to the compositions and methods of making such compositions, products that include such compositions are also provided.

SUMM As an embodiment of the present invention, a \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, the \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule. The \*\*\*thiol\*\*\* ester molecules also have an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule. The \*\*\*thiol\*\*\* ester molecules also have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM In some aspects, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups ranging from 0 to 1.0. In some aspects, the \*\*\*thiol\*\*\* ester molecules have an average ranging from 1.5 to 9 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule. In some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM The amount of \*\*\*thiol\*\*\* sulfur or \*\*\*mercaptan\*\*\* sulfur contained within the \*\*\*thiol\*\*\* ester molecules can also vary. For example, in some embodiments, the \*\*\*thiol\*\*\* ester molecules have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. In other embodiments, the \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur. In some embodiments, the \*\*\*thiol\*\*\* ester molecules have an average of less than 30 mole percent sulfur, which is present as cyclic sulfides. Alternatively, the \*\*\*thiol\*\*\* ester molecules have an average of less than 2 mole percent sulfur present as cyclic sulfides.

SUMM In some embodiments, the \*\*\*thiol\*\*\* ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the \*\*\*thiol\*\*\* ester molecules contain sulfur.

SUMM In addition to the \*\*\*thiol\*\*\* ester composition, a process for producing the \*\*\*thiol\*\*\* ester composition is advantageously provided as another embodiment of the present invention. To produce the \*\*\*thiol\*\*\* ester composition, hydrogen sulfide is contacted with an unsaturated ester composition. The unsaturated ester composition includes unsaturated esters that have an average of at least 1.5 ester groups per unsaturated ester molecule. The unsaturated esters also have an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are reacted to produce or form the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition advantageously includes \*\*\*thiol\*\*\* ester molecules that have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM Another process for producing the \*\*\*thiol\*\*\* ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, the hydrogen sulfide and the unsaturated ester composition are contacted. The unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are then reacted in a substantial absence of a solvent to form the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules. The \*\*\*thiol\*\*\* ester composition advantageously includes \*\*\*thiol\*\*\* ester molecules that have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than

### 1.5.

SUMM The resulting \*\*\*thiol\*\*\* ester molecules produced by this process possess advantageous characteristics. For example, in some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds of greater than 2. As another example, in other embodiments, the \*\*\*thiol\*\*\* ester molecules have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. In some aspects, greater than 40 percent of the \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur.

SUMM As another embodiment of the present invention, another process for preparing the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, a polyol composition and a thiolcarboxylic acid composition are contacted and reacted to produce the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules having an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

SUMM In addition to the \*\*\*thiol\*\*\* ester composition, other compositions are advantageously provided as embodiments of the present invention. For example, a hydroxy \*\*\*thiol\*\*\* ester composition is provided as another embodiment of the present invention. The hydroxyl \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at least 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

SUMM As described herein, the .alpha.-hydroxy \*\*\*thiol\*\*\* groups contain an alcohol or hydroxy group and a \*\*\*thiol\*\*\* group within the same group. In embodiments of the present invention, the .alpha.-hydroxy \*\*\*thiol\*\*\* groups can be replaced with separate alcohol and groups. In these embodiments, the same number of .alpha.-hydroxy groups can be used for the separate alcohol and groups. For example, in some embodiments, the

hydroxy        \*\*\*thiol\*\*\*    ester molecules have an average of at least 1.5  
                 .alpha.-hydroxy        \*\*\*thiol\*\*\*    groups. In embodiments that  
contain        separate alcohol and        \*\*\*thiol\*\*\*    groups, the hydroxy  
\*\*\*thiol\*\*\*  
                 ester molecules would contain an average of at least 1.5 alcohol  
groups        and an average of at least 1.5        \*\*\*thiol\*\*\*    groups.

SUMM        In some aspects, the hydroxy        \*\*\*thiol\*\*\*    ester molecules  
have an        average ranging from 1.5 to 9 .alpha.-hydroxy        \*\*\*thiol\*\*\*  
groups per        hydroxy        \*\*\*thiol\*\*\*    ester molecule. In some embodiments, the  
                 \*\*\*thiol\*\*\*    ester molecules have a molar ratio of carbon-  
carbon double        bonds to        \*\*\*thiol\*\*\*    groups of less than 1.5.

SUMM        In some embodiments, the        \*\*\*thiol\*\*\*    ester molecules are  
produced        from unsaturated esters that have an average of less than 25  
weight        percent of side chains that include 3 contiguous methylene  
interrupted        carbon-carbon double bonds. In another aspect, greater than 40  
percent        of the total side chains contained within the .alpha.-hydroxy  
                 \*\*\*thiol\*\*\*    ester molecules contain sulfur.

SUMM        The amount of        \*\*\*thiol\*\*\*    sulfur contained within the  
hydroxy        \*\*\*thiol\*\*\*    ester molecules can also vary. For example, in  
some        embodiments, the hydroxy        \*\*\*thiol\*\*\*    ester molecules have an  
average        of greater than 5 weight percent        \*\*\*thiol\*\*\*    sulfur. In other  
embodiments, the hydroxy        \*\*\*thiol\*\*\*    ester molecules have an  
average        ranging from 8 to 10 weight percent        \*\*\*thiol\*\*\*    sulfur.

SUMM        In some embodiments, the hydroxy        \*\*\*thiol\*\*\*    ester molecules  
have a        molar ratio of        \*\*\*epoxide\*\*\*    groups to the .alpha.-hydroxy  
                 \*\*\*thiol\*\*\*    groups of less than 2. In other aspects, the  
composition        is substantially free of        \*\*\*epoxide\*\*\*    groups.

SUMM        In addition to the hydroxy        \*\*\*thiol\*\*\*    ester composition,  
methods        or processes for making the hydroxy        \*\*\*thiol\*\*\*    ester  
composition        are advantageously provided as embodiments of the present  
invention. In  
                 an embodiment, a process for preparing the hydroxy        \*\*\*thiol\*\*\*  
ester        composition is provided that includes the step of contacting the  
                 hydrogen sulfide and an epoxidized unsaturated ester composition.

The        epoxidized unsaturated ester composition includes epoxidized

unsaturated  
 esters having an average of at least 1.5 ester groups per  
 epoxidized  
 unsaturated ester molecule and having an average of at least 1.5  
 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester  
 molecule. The  
 hydrogen sulfide and the epoxidized unsaturated esters are then  
 reacted  
 to form the hydroxy \*\*\*thiol\*\*\* ester composition.

SUMM In some embodiments, a molar ratio of the hydrogen sulfide to  
 \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated esters is  
 greater  
 than 1.

SUMM Another process for preparing the hydroxy \*\*\*thiol\*\*\* ester  
 composition is advantageously provided as another embodiment of  
 the  
 present invention. In this process embodiment, a polyol  
 composition and  
 a hydroxy \*\*\*thiol\*\*\* carboxylic acid composition are  
 contacted and  
 reacted to produce the hydroxy \*\*\*thiol\*\*\* ester composition.

In  
 this embodiment, the hydroxy \*\*\*thiol\*\*\* ester composition  
 includes  
 hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at  
 least  
 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and  
 having  
 an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups  
 per  
 hydroxy \*\*\*thiol\*\*\* ester molecule.

SUMM A cross-linked \*\*\*thiol\*\*\* ester composition is  
 advantageously  
 provided as another embodiment of the present invention. The  
 cross-linked \*\*\*thiol\*\*\* ester composition includes  
 \*\*\*thiol\*\*\*  
 ester oligomers having at least two \*\*\*thiol\*\*\* ester  
 monomers  
 connected by a polysulfide linkage having a structure -S.sub.Q-,  
 wherein  
 Q is greater than 1. In some embodiments, the \*\*\*thiol\*\*\*  
 ester  
 oligomers have at least three \*\*\*thiol\*\*\* ester monomers  
 connected  
 by polysulfide linkages. In another aspect, the \*\*\*thiol\*\*\*  
 ester  
 oligomers have from 3 to 20 \*\*\*thiol\*\*\* ester monomers  
 connected by  
 polysulfide linkages.

SUMM In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition  
 includes both \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\*  
 ester  
 oligomers. In some embodiments, the \*\*\*thiol\*\*\* ester  
 monomers and  
 \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\*  
 sulfur

content ranging from 0.5 to 8 weight percent; or alternatively, ranging from 8 to 15 weight percent. The combined \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers can have an average molecular weight greater than 2000; or alternatively, in a range from 2000 to 20,000.

SUMM As another embodiment of the present invention, a cross-linked \*\*\*thiol\*\*\* ester composition produced by the process comprising the steps of contacting the \*\*\*thiol\*\*\* ester composition with an oxidizing agent and reacting the \*\*\*thiol\*\*\* ester and the oxidizing agent to form \*\*\*thiol\*\*\* ester oligomers is advantageously provided. In this embodiment, the \*\*\*thiol\*\*\* ester oligomers have at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure  $-S_{\text{sub.Q-}}$ , wherein Q is greater than 1.

SUMM A process to produce the cross-linked \*\*\*thiol\*\*\* ester composition is also advantageously provided as another embodiment of the present invention. In this process, a \*\*\*thiol\*\*\* ester composition is contacted and reacted with an oxidizing agent to form \*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure  $-S_{\text{sub.Q-}}$ , wherein Q is greater than 1. In some embodiments, the oxidizing agent is elemental sulfur, oxygen, or hydrogen peroxide. In an aspect, the oxidizing agent is elemental sulfur.

SUMM In an aspect, the \*\*\*thiol\*\*\* ester is a hydroxy \*\*\*thiol\*\*\* ester. In other aspects, a weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester molecules ranges from 0.5 to 32.

SUMM The step of the reacting the \*\*\*thiol\*\*\* ester and the oxidizing agent can be performed at a temperature ranging from 25.degree.

C. to 150.degree. C. The process for producing the cross-linked \*\*\*thiol\*\*\* ester composition can also include the step of stripping residual hydrogen sulfide from the cross-linked \*\*\*thiol\*\*\* ester composition produced. In another aspect, the reaction of the \*\*\*thiol\*\*\* ester and the elemental sulfur is catalyzed. In some embodiments, the catalyst is an amine.

SUMM In another of its aspects, the present invention relates to a controlled release fertilizer material comprising a particulate plant nutrient surrounded by a coating which is the reaction product of a mixture comprising: (i) a first component selected from an isocyanate and/or an epoxy resin, and (ii) a first active hydrogen-containing compound selected from the group consisting of: a \*\*\*thiol\*\*\* ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester composition and mixtures thereof.

SUMM In another of its aspects, the present invention relates to a process for the production of abrasion resistant polythiourethane and/or epoxy polymer encapsulated controlled release fertilizer particles by incorporating in urethane and/or epoxy polymer forming reaction mixture a sulfur-containing compound such as one or more of a \*\*\*thiol\*\*\* ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester composition, other sulfur-based compounds described herein below and mixtures thereof.

SUMM Preferably, for the production of the present polythiourethane encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a \*\*\*thiol\*\*\* ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil. In one preferred embodiment, the sulfur-containing vegetable oil comprises a mercaptanized (MVO), more preferably as described in more detail herein, even more preferably an MVO produced by the addition of hydrogen sulfide to a vegetable oil. In another preferred embodiment, the sulfur-containing vegetable oil comprises mercapto-hydroxy vegetable oil (MHVO), more preferably as described in more detail herein, even more preferably an MHVO produced by the addition of hydrogen sulfide to epoxidized vegetable oil. In yet another preferred embodiment, the sulfur containing vegetable oil comprises sulfur cross-linked mercaptanized vegetable oil (CMVO), more preferably as described in more detail



herein, even more preferably an CMVO produced by the addition of elemental sulfur to mercaptanized vegetable oil (MVO).

SUMM Preferably, for the production of epoxy polymer encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a \*\*\*thiol\*\*\* ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil (e.g., MVO and/or MHVO and/or CMVO) is used as one of the epoxy resin-reactive components.

DRWD FIG. 1 includes two graphs that compare the NMR's of soybean oil, which is shown in the top graph, and a \*\*\*thiol\*\*\* containing ester produced from soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 2 includes two graphs that compare the NMR's of epoxidized soybean oil, which is shown in the top graph, and a \*\*\*thiol\*\*\* containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 3 is a gas chromatograph (GC)/mass spectrometer (MS) trace of a \*\*\*thiol\*\*\* containing ester that was produced from soybean oil in accordance with an embodiment of the present invention and then treated by methanolysis;

DRWD FIG. 5 is a GC/MS trace of hydroxy \*\*\*thiol\*\*\* containing ester produced from epoxidized soybean oil in accordance with an embodiment of

the present invention and then treated by methanolysis;  
DETD In this specification, " \*\*\*thiol\*\*\* ester composition" refers to an ester composition that includes " \*\*\*thiol\*\*\* ester molecules." The

\*\*\*thiol\*\*\* ester molecule has at least one \*\*\*thiol\*\*\* group and at least one ester group within the \*\*\*thiol\*\*\* ester molecule.

DETD In this specification, "hydroxy \*\*\*thiol\*\*\* ester composition" refers to an ester composition that includes "hydroxy

\*\*\*thiol\*\*\* ester molecules." The hydroxy \*\*\*thiol\*\*\* ester molecule has at least one \*\*\*thiol\*\*\* group, at least one ester group, and at least one hydroxy or alcohol group within the hydroxy \*\*\*thiol\*\*\*

ester molecule. Alternatively, the alcohol group and the \*\*\*thiol\*\*\* group can be combined in the same group, which is referred to as an ".alpha.-hydroxy \*\*\*thiol\*\*\* group."

DETD In this specification, "polythiourethane" refers to a urethane composition that includes more than one of the following structure:

##STR1## The presence of the thiourethane group can be determined by method known to those skilled in the art (for example infrared spectroscopy, Raman spectroscopy, and/or NMR). \*\*\*Thiol\*\*\*

Ester Composition

DETD The present invention advantageously provides a \*\*\*thiol\*\*\* ester composition as an embodiment of the present invention. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule. The \*\*\*thiol\*\*\* ester composition also has a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5, as described herein.

DETD Generally, the \*\*\*thiol\*\*\* ester composition contains molecules having at least one ester group and at least one \*\*\*thiol\*\*\* group.

The \*\*\*thiol\*\*\* ester composition of this invention can be produced from any unsaturated ester, as described herein. Because the feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule, carbon-carbon double bond reactivity and statistical probability dictate that each \*\*\*thiol\*\*\* ester molecule of the \*\*\*thiol\*\*\* ester composition produced from the unsaturated ester composition will not have the same number of \*\*\*thiol\*\*\* groups, number of unreacted carbon-carbon double bonds, number of cyclic sulfides, molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* groups, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups and other quantities of functional groups and molar ratios disclosed herein as the feedstock unsaturated ester. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Thus, many of these properties will be discussed as an average number of the groups per \*\*\*thiol\*\*\* ester molecule

within the \*\*\*thiol\*\*\* ester composition or average ratio per  
 \*\*\*thiol\*\*\* ester molecule within the \*\*\*thiol\*\*\* ester composition. In  
 other embodiments, it is desired to control the content of  
 \*\*\*thiol\*\*\* sulfur present in the \*\*\*thiol\*\*\* ester. Because it is  
 difficult to ensure that the hydrogen sulfide reacts with every carbon-carbon  
 double bond within the unsaturated ester, certain molecules of  
 \*\*\*thiol\*\*\* ester can have more or less \*\*\*thiol\*\*\* groups than other  
 molecules. Thus, the weight percent of \*\*\*thiol\*\*\* groups is stated as  
 an average across all \*\*\*thiol\*\*\* ester molecules of the  
 \*\*\*thiol\*\*\* ester composition.  
 DETD The \*\*\*thiol\*\*\* ester can be derived from any unsaturated  
 ester described herein.  
 DETD The \*\*\*thiol\*\*\* ester compositions can be described as  
 comprising one or more separate or discreet functional groups of the  
 \*\*\*thiol\*\*\* ester molecule and/or \*\*\*thiol\*\*\* ester composition. These  
 independent functional groups can include: the number of (or  
 average number of) ester groups per \*\*\*thiol\*\*\* ester molecule,  
 \*\*\*thiol\*\*\* containing the number of (or average number of)  
 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule, the  
 number of (or average number of) unreacted carbon-carbon double bonds per  
 \*\*\*thiol\*\*\* ester molecule, the average \*\*\*thiol\*\*\*  
 sulfur content of the \*\*\*thiol\*\*\* ester composition, the percentage (or  
 average percentage) of sulfide linkages per \*\*\*thiol\*\*\* ester  
 molecule, and the percentage (or average percentage) of cyclic sulfide groups  
 per \*\*\*thiol\*\*\* ester molecule. Additionally, the \*\*\*thiol\*\*\*  
 ester compositions can be described using individual or a combination  
 of ratios including the ratio of double bonds to \*\*\*thiol\*\*\*  
 groups, the ratio of cyclic sulfides to \*\*\*mercaptan\*\*\* group, and  
 the like. As separate elements, these functional groups of the  
 \*\*\*thiol\*\*\* composition will be described separately.  
 DETD Minimally, in some embodiments, the \*\*\*thiol\*\*\* ester  
 contains \*\*\*thiol\*\*\* ester molecules having at least one ester group  
 and one \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester molecule. As the  
 \*\*\*thiol\*\*\* ester is prepared from unsaturated esters, the

\*\*\*thiol\*\*\* ester can contain the same number of ester groups as the unsaturated esters described herein. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule. Alternatively, the \*\*\*thiol\*\*\* ester molecules have an average of at least 2 ester groups per \*\*\*thiol\*\*\* ester molecule, alternatively, an average of at least 2.5 ester groups per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 ester groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments, the \*\*\*thiol\*\*\* esters have an average of from 1.5 to 8 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 7 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2.5 to 5 ester groups per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 3 to 4 ester groups per \*\*\*thiol\*\*\* ester molecule. In yet other embodiments, the \*\*\*thiol\*\*\* ester comprises an average of 3 ester groups per \*\*\*thiol\*\*\* ester molecule or alternatively, an average of 4 ester groups per unsaturated ester molecule.

DETD Minimally, the \*\*\*thiol\*\*\* ester comprises an average of at least one \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester molecule. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule; alternatively, \*\*\*thiol\*\*\* containing an average of at least 2 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments, the \*\*\*thiol\*\*\* ester molecules have an average of from 1.5 to 9 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 3 to 8 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule; alternatively, \*\*\*thiol\*\*\* containing an average of from 2 to 4 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule, or alternatively, an average of from 4 to 8 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

DETD In other embodiments, the \*\*\*thiol\*\*\* ester can be described

by the average amount of \*\*\*thiol\*\*\* sulfur present in \*\*\*thiol\*\*\* ester. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of at least 5 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 10 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule, or alternatively, an average of greater than 15 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of from 5 to 25 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 5 to 20 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 6 to 15 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule.

DETD Generally, the location of the \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester is not particularly important and will be dictated by the method used to produce the \*\*\*thiol\*\*\* ester. In embodiments wherein the \*\*\*thiol\*\*\* ester is produced by contacting an unsaturated ester, the position of the \*\*\*thiol\*\*\* group will be dictated by the position of the carbon-carbon double bond. When the carbon-carbon double bond is an internal carbon-carbon double bond, the method of producing the \*\*\*thiol\*\*\* ester will result in a secondary \*\*\*thiol\*\*\* group. However, when the double bond is located at a terminal position it is possible to choose reaction conditions to produce a \*\*\*thiol\*\*\* ester comprising either a primary \*\*\*thiol\*\*\* group or a secondary \*\*\*thiol\*\*\* group.

DETD Some methods of producing the \*\*\*thiol\*\*\* ester composition can additionally create sulfur containing functional groups other than a \*\*\*thiol\*\*\* group. For example, in some \*\*\*thiol\*\*\* ester production methods, an introduced \*\*\*thiol\*\*\* group can react with a carbon-carbon double bond within the same unsaturated ester to produce a sulfide linkage. When the reaction is with a double bond of a second unsaturated ester, this produces a simple sulfide linkage. However, in some instances, the second carbon-carbon double bond is located in the

same unsaturated ester molecule. When the \*\*\*thiol\*\*\* group reacts with a second carbon-carbon double bond within the same unsaturated ester molecule, a sulfide linkage is produced. In some instances, the carbon-carbon double bond can be within a second ester group of the unsaturated ester molecule. While in other instances, the carbon-carbon double bond can be within the same ester group of the unsaturated ester molecule.

DETD When the \*\*\*thiol\*\*\* group reacts with the carbon-carbon double bond in a second ester group of the same unsaturated ester molecule, the cyclic sulfide would contain two ester groups contained within a ring structure. When the \*\*\*thiol\*\*\* group reacts with the carbon-carbon double bond within the same ester group, the cyclic sulfide would not contain an ester group within the ring structure. Within this specification, this second type of cyclic sulfide is referred to as a cyclic sulfide. Within this specification, the first type of cyclic sulfide is referred to as a simple sulfide. In the cyclic sulfide case, the sulfide linkage produces a cyclic sulfide functionality within a single ester group of the \*\*\*thiol\*\*\* ester. This linkage is termed a cyclic sulfide for purposes of this application. One such sulfide group that can be produced is a cyclic sulfide. The cyclic sulfide rings that can be produced include a tetrahydrothiopyran ring, a thietane ring, or a thiophane ring (tetrahydrothiophene ring).

DETD In some embodiments, it is desirable to control the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* ester. In an embodiment the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* ester molecules comprises less than 30 mole percent. Alternatively, the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* esters comprises less than 20 mole percent; alternatively, less than 10 mole percent; alternatively, less than 5 mole percent; or alternatively, less than 2 mole percent. In other embodiments, it is desired to control the molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups. In other embodiments, it is desirable to have

molar ratios of cyclic sulfide to \*\*\*thiol\*\*\* group. In an embodiment, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester is less than 1.5. Alternatively, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester is less than 1; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, 0.1. In some embodiments, the ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester ranges from 0 to 1; or alternatively, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester ranges between 0.05 and 1.

DETD In some instances it can be desirable to have carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester composition while in other embodiments it can be desirable to minimize the number of carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester composition.

The presence of carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester can be stated as an average molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* -sulfur. In an embodiment, the average ratio of the remaining unreacted carbon-carbon double bond in the \*\*\*thiol\*\*\* ester composition to \*\*\*thiol\*\*\* sulfur is less than 1.5 per \*\*\*thiol\*\*\* ester molecule. Alternatively, the average ratio of carbon-carbon double bond to \*\*\*thiol\*\*\* sulfur is less than 1.2 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 1.0 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.75 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.5 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.2 per \*\*\*thiol\*\*\* ester molecule; or alternatively, less than 0.1 per \*\*\*thiol\*\*\* ester molecule.

DETD In particular embodiments, the \*\*\*thiol\*\*\* ester is produced from unsaturated ester compositions. Because the feedstock unsaturated ester has particular compositions having a certain number of ester groups present, the product \*\*\*thiol\*\*\* ester composition will have about the same number of ester groups per \*\*\*thiol\*\*\* ester molecule as the feedstock unsaturated ester. Other, independent \*\*\*thiol\*\*\* ester properties described herein can be used to further describe the \*\*\*thiol\*\*\* ester composition.

DETD In some embodiments, the \*\*\*thiol\*\*\* ester molecules are produced from unsaturated esters having an average of less than 25 weight

percent of side chains having 3 contiguous methylene interrupted carbon-carbon double bonds, as described herein. In some embodiments, greater than 40 percent of the \*\*\*thiol\*\*\* containing natural source total side chains can include sulfur. In some embodiments, greater than 60 percent of the \*\*\*thiol\*\*\* ester molecule total side chains can include sulfur. In other embodiments, greater than 50, 70, or 80 percent of the \*\*\*thiol\*\*\* ester molecule total side chains can include sulfur.

DETD In an embodiment, the \*\*\*thiol\*\*\* ester is a \*\*\*thiol\*\*\* containing natural source oil, as described herein. When the \*\*\*thiol\*\*\* ester is a \*\*\*thiol\*\*\* containing natural source oil, functional groups that are present in the \*\*\*thiol\*\*\* containing natural source oil can be described in a "per \*\*\*thiol\*\*\* ester molecule" basis or in a "per triglyceride" basis. The \*\*\*thiol\*\*\* containing natural source oil can have substantially the same properties as the \*\*\*thiol\*\*\* ester composition, such as the molar ratios and other independent descriptive elements described herein.

DETD The average number of \*\*\*thiol\*\*\* groups per triglyceride in the \*\*\*thiol\*\*\* containing natural source oil is greater than about 1.5. In some embodiments, the average number of \*\*\*thiol\*\*\* groups per triglyceride can range from about 1.5 to about 9.

DETD The \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an unsaturated ester composition and can be further limited by the process as described herein. The \*\*\*thiol\*\*\* containing natural source oil can also be described using a molecular weight or an average molecular weight of the side chains.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester Composition

DETD In embodiments of the present invention, the \*\*\*thiol\*\*\* ester compositions can also contain a hydroxy or alcohol group. When the \*\*\*thiol\*\*\* ester composition includes the hydroxy group, the \*\*\*thiol\*\*\* ester composition is referred to herein as the hydroxy \*\*\*thiol\*\*\* ester composition. The quantity or number of alcohol groups present in the hydroxy \*\*\*thiol\*\*\* ester composition can be



independent of the quantity of other functional groups present in the hydroxy \*\*\*thiol\*\*\* ester composition (i.e. \*\*\*thiol\*\*\* groups, ester groups, sulfides, cyclic sulfides). Additionally, the weight percent of \*\*\*thiol\*\*\* sulfur and functional group ratios (i.e. molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups and other disclosed quantities of functional groups and their molar ratios to the \*\*\*thiol\*\*\* groups) are separate or discreet elements that can be used to describe the hydroxy \*\*\*thiol\*\*\* ester composition. The hydroxy \*\*\*thiol\*\*\* ester composition can be described using any combination of the hydroxy \*\*\*thiol\*\*\* ester composition separate functional groups or ratios described herein. In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester composition is produced by reacting hydrogen sulfide with an epoxidized unsaturated ester composition as described herein. Because the epoxidized unsaturated ester can contain multiple \*\*\*epoxide\*\*\* groups, \*\*\*epoxide\*\*\* group reactivity and statistical probability dictate that not all hydroxy \*\*\*thiol\*\*\* ester molecules of the hydroxy \*\*\*thiol\*\*\* ester composition will have the same number of hydroxy groups, \*\*\*thiol\*\*\* groups, .alpha.-hydroxy \*\*\*thiol\*\*\* groups, sulfides, cyclic sulfides, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups, weight percent \*\*\*thiol\*\*\* sulfur and other disclosed quantities of functional groups and their molar ratios as the epoxidized unsaturated ester composition. Thus, many of these properties will be discussed as an average number or ratio per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, it is desired to control the content of \*\*\*thiol\*\*\* sulfur present in the hydroxy \*\*\*thiol\*\*\* ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every \*\*\*epoxide\*\*\* group within

the epoxidized unsaturated ester, certain hydroxy \*\*\*thiol\*\*\*  
ester molecules can have more or less \*\*\*thiol\*\*\* groups than other  
molecules within the hydroxy \*\*\*thiol\*\*\* ester composition.  
Thus, the weight percent of \*\*\*thiol\*\*\* groups can be stated as an  
average weight percent across all hydroxy \*\*\*thiol\*\*\* ester  
molecules.  
DETD As an embodiment of the present invention, the hydroxy  
\*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester  
molecules that have an average of at least 1 ester groups and an average of at  
least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\*  
ester molecule. As an embodiment of the present invention, the hydroxy  
\*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\*  
ester molecules that have an average of at least 1.5 ester groups and  
an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups  
per hydroxy \*\*\*thiol\*\*\* ester molecule.  
DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\*  
ester comprises at least one ester, at least one \*\*\*thiol\*\*\* group,  
and at least one hydroxy group. Because the hydroxy \*\*\*thiol\*\*\*  
ester is prepared from epoxidized unsaturated esters, the hydroxy  
\*\*\*thiol\*\*\* ester can contain the same number of ester groups as the  
epoxidized unsaturated esters. In an embodiment, the hydroxy \*\*\*thiol\*\*\*  
ester molecules have an average of at least 1.5 ester groups per  
hydroxy \*\*\*thiol\*\*\* ester molecule. Alternatively, the hydroxy  
\*\*\*thiol\*\*\* ester molecules have an average of at least 2 ester groups per  
hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at  
least 2.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
alternatively, an average of at least 3 ester groups per hydroxy  
\*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy  
\*\*\*thiol\*\*\* esters have an average of from 1.5 to 8 ester  
groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
of from 2 to 7 ester groups per hydroxy \*\*\*thiol\*\*\* ester  
molecule; alternatively, an average of from 2.5 to 5 ester groups per  
hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
from 3 to 4 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In yet  
other

embodiments, the .alpha.-hydroxy \*\*\*thiol\*\*\* ester comprises an average of 3 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule or alternatively, an average of 4 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD In some embodiments, the hydroxy group and the \*\*\*thiol\*\*\* group are combined in the same group, which produces the .alpha.-hydroxy \*\*\*thiol\*\*\* group. In other embodiments, the \*\*\*thiol\*\*\* group and the hydroxy or alcohol group are not in the same group. When this occurs, to produce the hydroxy \*\*\*thiol\*\*\* ester composition, the alcohol group is added independently of the \*\*\*thiol\*\*\* group. For example, as another embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition advantageously includes hydroxy \*\*\*thiol\*\*\* ester molecules. The hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 ester groups, an average of at least 1.5 \*\*\*thiol\*\*\* groups, and an average of at least 1.5 alcohol groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester comprises at least one \*\*\*thiol\*\*\* group per hydroxy \*\*\*thiol\*\*\* ester molecule. In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of from 1.5 to 9 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 4 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 4 to 8 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester.

DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester

composition comprises an average of at least 1 hydroxy or alcohol group per hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition comprises an average of at least 1.5 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, average of at least 2 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 hydroxy groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments, the \*\*\*thiol\*\*\* ester composition comprises an average of from 1.5 to 9 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 3 to 8 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 4 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 4 to 8 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD In yet other embodiments, the number of hydroxy groups can be stated as an average molar ratio of hydroxy group to \*\*\*thiol\*\*\* groups. Minimally, in some embodiments, the molar ratio of hydroxy groups to \*\*\*thiol\*\*\* groups is at least 0.25. In some embodiments, the molar ratio of hydroxy groups to \*\*\*thiol\*\*\* groups is at least 0.5; alternatively, at least 0.75; alternatively, at least 1.0; alternatively, at least 1.25; or alternatively, at least 1.5. In other embodiments, the molar ratio of hydroxy groups to \*\*\*thiol\*\*\* groups ranges from 0.25 to 2.0; alternatively, from 0.5 to 1.5; or alternatively, from 0.75 to 1.25.

DETD In embodiments where the hydroxy \*\*\*thiol\*\*\* esters are produced from an epoxidized unsaturated ester, the hydroxy \*\*\*thiol\*\*\* esters can be described as containing ester groups and .alpha.-hydroxy \*\*\*thiol\*\*\* groups. The number of ester groups and the number of .alpha.-hydroxy \*\*\*thiol\*\*\* groups are independent elements and as such the hydroxy \*\*\*thiol\*\*\* esters can be described as having any combination of ester groups and .alpha.-hydroxy \*\*\*thiol\*\*\* groups described herein. Minimally, the hydroxy \*\*\*thiol\*\*\* ester comprises an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* group per

hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition comprises an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 .alpha.-hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy ester composition comprises an average of from 1.5 to 9 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 3 to 8 .alpha.-hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 4 .alpha.-hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 4 to 8 .alpha.-hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD The hydroxy \*\*\*thiol\*\*\* esters can be produced by contacting an epoxidized ester derived from an unsaturated ester (i.e., unsaturated ester), as described herein. In some instances it can be desirable to have \*\*\*epoxide\*\*\* groups present in the hydroxy \*\*\*thiol\*\*\* ester composition. While in other embodiments, it can be desirable to minimize the number of epoxy groups present in the hydroxy \*\*\*thiol\*\*\* ester composition. Thus, the presence of residual \*\*\*epoxide\*\*\* groups can be another separate functional group used to describe the hydroxy \*\*\*thiol\*\*\* ester.

DETD The presence of \*\*\*epoxide\*\*\* groups in the hydroxy \*\*\*thiol\*\*\* ester can be independently described as an average number of \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester, a molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, a molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups, or any combination thereof. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules comprise an average of less than 2 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule, i.e., the hydroxy \*\*\*thiol\*\*\* ester molecules have a molar ratio of

\*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups of less than 2.  
 Alternatively, the hydroxy \*\*\*thiol\*\*\* ester comprises an  
 average of less than 1.5 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\*  
 ester molecule; alternatively, an average of less than 1  
 \*\*\*epoxide\*\*\* group per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively,  
 an average of less than 0.75 \*\*\*epoxide\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
 less than 0.5 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule.  
 In other embodiments, the molar ratio of \*\*\*epoxide\*\*\* groups  
 to \*\*\*thiol\*\*\* groups averages less than 1.5. Alternatively, the  
 molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups  
 averages less than 1; alternatively, averages less than 0.75;  
 alternatively, averages less than 0.5; alternatively, averages less than 0.25;  
 or alternatively, averages less than 0.1. In yet other embodiments,  
 the molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy  
 \*\*\*thiol\*\*\* groups averages less than 1.5. Alternatively, the molar ratio of  
 \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\*  
 groups averages less than 1; alternatively, averages less than 0.75;  
 alternatively, averages less than 0.5; alternatively, averages  
 less than 0.25; or alternatively, averages less than 0.1.  
 DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester  
 composition is substantially free of \*\*\*epoxide\*\*\* groups.  
 DETD In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester can be  
 described by the average amount of \*\*\*thiol\*\*\* sulfur present  
 in hydroxy \*\*\*thiol\*\*\* ester. In an embodiment, the hydroxy  
 \*\*\*thiol\*\*\* ester molecules have an average of at least 2.5  
 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester  
 molecule; alternatively, an average of at least 5 weight percent  
 \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an average of greater than 15 weight percent \*\*\*thiol\*\*\* sulfur  
 per hydroxy \*\*\*thiol\*\*\* ester molecule. In an embodiment, the  
 hydroxy \*\*\*thiol\*\*\* ester molecules have an average of from 5 to 25  
 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester

molecule; alternatively, an average of from 5 to 20 weight percent

percent      \*\*\*thiol\*\*\*      sulfur per hydroxy      \*\*\*thiol\*\*\*      ester molecule;

alternatively, an average of from 6 to 15 weight percent

\*\*\*thiol\*\*\*      sulfur per hydroxy      \*\*\*thiol\*\*\*      ester molecule; or

alternatively, an average of from 8 to 10 weight percent      \*\*\*thiol\*\*\*      sulfur per hydroxy      \*\*\*thiol\*\*\*      ester molecule.

DETD      In some embodiments, at least 20 percent of the total side chains

include the .alpha.-hydroxy      \*\*\*thiol\*\*\*      group. In some embodiments,

at least 20 percent of the total side chains include the .alpha.-hydroxy      \*\*\*thiol\*\*\*      group. In some embodiments, at least 60 percent of the

total side chains include the .alpha.-hydroxy      \*\*\*thiol\*\*\*      group;

alternatively, at least 70 percent of the total side chains include the

.alpha.-hydroxy      \*\*\*thiol\*\*\*      group. Yet in other embodiments, at

least 80 percent of the total side chains include the .alpha.-hydroxy      \*\*\*thiol\*\*\*      group.

DETD      In some aspects, greater than 20 percent of the hydroxy \*\*\*thiol\*\*\*

ester molecule total side chains contain sulfur. In some aspects, greater than 40 percent of the hydroxy      \*\*\*thiol\*\*\*      ester molecule

total side chains contain sulfur. In some aspects, greater than 60

percent of the hydroxy      \*\*\*thiol\*\*\*      ester molecule total side chains

contain sulfur; alternatively, greater than 70 percent of the total side

chains contain sulfur; or alternatively, greater than 80 percent of the

total side chains contain sulfur.

DETD      In particular embodiments, the epoxidized unsaturated ester used in the

synthesis of the hydroxy      \*\*\*thiol\*\*\*      ester is produced from the

epoxidized unsaturated ester composition that includes an epoxidized

natural source oil. Because the natural source oils have particular

compositions regarding the number of ester groups present, the hydroxy

\*\*\*thiol\*\*\*      ester will have about the same number of ester groups as

the feedstock natural source oil. Other independent properties that are

described herein can be used to further describe the hydroxy      \*\*\*thiol\*\*\*      ester.

DETD      In other embodiments, the epoxidized unsaturated ester used to produce

the hydroxy      \*\*\*thiol\*\*\*      ester is produced from synthetic (or

semi-synthetic) unsaturated ester oils. Because the synthetic ester oils can have particular compositions regarding the number of ester groups present, the hydroxy \*\*\*thiol\*\*\* ester would have about the same number of ester groups as the synthetic ester oil. Other, independent properties of the unsaturated ester, whether the unsaturated ester includes natural source or synthetic oils, can be used to further describe the hydroxy \*\*\*thiol\*\*\* ester composition.

DETD The hydroxy \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an epoxidized unsaturated ester composition and can be further limited by the process as described herein. The hydroxy \*\*\*thiol\*\*\* containing natural source oil can also be described using an average molecular weight or an average molecular weight of the side chains.

DETD Cross-Linked \*\*\*Thiol\*\*\* Ester Compositions

DETD In an aspect, the present invention relates to a cross-linked \*\*\*thiol\*\*\* ester composition. Generally, the cross-linked \*\*\*thiol\*\*\* ester molecules are oligomers of \*\*\*thiol\*\*\* esters that are connected together by polysulfide linkages -S.sub.x- wherein x is an integer greater 1. As the cross-linked \*\*\*thiol\*\*\* ester is described as an oligomer of \*\*\*thiol\*\*\* esters, the \*\*\*thiol\*\*\* esters can be described as the monomer from which the cross-linked \*\*\*thiol\*\*\* esters are produced.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure -S.sub.Q-, wherein Q is an integer greater than 1. In an aspect, the polysulfide linkage may be the polysulfide linkage -S.sub.Q-, wherein Q is 2, 3, 4, or mixtures thereof. In other embodiments, Q can be 2; alternatively, 3; or alternatively, 4.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having at least 3 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, 5 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, 7 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; or alternatively, 10 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages. In yet other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having from 3 to 20 \*\*\*thiol\*\*\* ester



monomers connected by polysulfide linkages; alternatively, from 5 to 15 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; or alternatively, from 7 to 12 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight greater than 2,000. In other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight greater than 5,000; or alternatively, greater than 10,000. In yet other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight ranging from 2,000 to 20,000; alternatively, from 3,000 to 15,000; or alternatively, from 7,500 to 12,500.

DETD In an aspect, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content greater than 0.5. In other embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content greater than 1; alternatively, greater than 2; alternatively, greater than 4. In yet other embodiments, the \*\*\*thiol\*\*\* ester monomers and the \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content from 0.5 to 8; alternatively, from 4 to 8; or alternatively, 0.5 to 4.

DETD In an aspect, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total sulfur content greater than 8. In some embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total sulfur content greater than 10; alternatively, greater than 12. In yet other embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total sulfur content ranging from 8 to 15 weight percent; alternatively, from 9 to 14; or alternatively, from 10 to 13.

DETD The cross-linked \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting a \*\*\*thiol\*\*\* ester with oxidizing agent and can be further limited by

the process as described herein.

DETD The present invention advantageously includes sulfide-containing ester compositions as embodiments of the present invention. Generally, the sulfide-containing ester compositions can be described as containing molecules having at least one ester group and a least one sulfide group within each molecule. The sulfide-containing esters used in the present invention can be produced by contacting either an unsaturated ester or an epoxidized unsaturated ester with a \*\*\*thiol\*\*\* containing compound as described herein.

DETD The feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule. The carbon-carbon double bond reactivity and statistical probability, however, dictate that each sulfide-containing ester molecule of the \*\*\*thiol\*\*\* - containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted carbon-carbon double bonds, molar ratio of carbon-carbon double bonds to sulfide groups, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Many of these properties are discussed herein as an average number of the groups per sulfide-containing ester molecule within the sulfide-containing ester composition or average ratio per \*\*\*thiol\*\*\* -containing ester molecule within the sulfide-containing ester composition.

DETD In embodiments related to the sulfide-containing ester that is produced from an epoxidized unsaturated ester, the feedstock epoxidized unsaturated esters can contain multiple \*\*\*epoxide\*\*\* groups per unsaturated ester molecule. Individual \*\*\*epoxide\*\*\* group reactivity and statistical probability dictate that each sulfide-containing ester molecule of the sulfide-containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted \*\*\*epoxide\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to sulfide groups, and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock epoxidized unsaturated esters can also comprise a mixture of individual

epoxidized  
unsaturated ester molecules having a different number of  
\*\*\*epoxide\*\*\*  
groups and/or ester groups. Thus, many of these properties are  
described  
as an average number of the groups per sulfide-containing ester  
molecules within the sulfide-containing ester composition or  
average  
ratio per \*\*\*thiol\*\*\* -containing ester molecule within the  
sulfide-containing ester composition.  
DETD Minimally, in some embodiments, the sulfide-containing esters  
comprise  
at least one ester group per sulfide-containing ester molecule.  
In some  
embodiments, the sulfide-containing ester has an average of at  
least 1.5  
ester groups per sulfide-containing ester molecule.  
Alternatively, the  
sulfide-containing ester molecules have an average of at least 2  
ester  
groups per sulfide-containing ester molecule; alternatively, an  
average  
of at least 2.5 ester groups per sulfide-containing ester  
molecule; or  
alternatively, an average of at least 3 ester groups per  
sulfide-containing ester molecule. In other embodiments, the  
sulfide-containing esters have an average of from 1.5 to 9 ester  
groups  
per sulfide-containing ester molecule; alternatively, an average  
of from  
1.5 to 8 ester groups per sulfide-containing ester molecule;  
alternatively, an average of from 2 to 8 ester groups per  
sulfide-containing ester molecule; alternatively, an average of  
from 2  
to 7 ester groups per sulfide-containing ester molecule;  
alternatively,  
an average of from 2.5 to 5 ester groups per sulfide-containing  
ester  
molecule; alternatively, an average of from 3 to 5 ester groups  
per  
sulfide-containing ester molecule; or alternatively, an average  
of from  
3 to 4 ester groups per sulfide-containing ester molecule. In yet  
other  
embodiments, the hydroxy \*\*\*thiol\*\*\* -containing ester  
comprises an  
average of about 3 ester groups per sulfide-containing ester  
molecule;  
or alternatively, an average of about 4 ester groups per  
sulfide-containing ester molecule.  
DETD In some embodiments, R.sup.3 comprises at least one functional  
group.  
In one aspect, the functional group is selected from the group  
consisting of a hydroxy group, a carboxylic acid group, a  
carboxylic  
ester group, an amine group, a sulfide group, and a second  
\*\*\*thiol\*\*\*  
group. In some aspects, R.sup.3 comprises at least two functional  
groups. In some aspects, the functional groups are selected from  
the

group consisting of a hydroxy group, carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, a second \*\*\*thiol\*\*\* group, and mixtures thereof.

DETD The sulfide-containing ester compositions can also be described as a product produced by the process comprising contacting an unsaturated ester with a \*\*\*mercaptan\*\*\* and can be further limited by the process as described herein. In other embodiments, the sulfide-containing ester composition can also be described as a product produced by a process comprising contacting an epoxidized unsaturated ester with a \*\*\*mercaptan\*\*\* and can be further limited by the process as described herein.

DETD Generally, the thioacrylate ester composition can be described as comprising thioacrylate molecules having at least one ester group in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule and at least one thioacrylate group. The ester group(s) that are in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule are hereinafter referred to as "supplementary ester group(s)." The thioacrylate ester composition described herein can be produced by contacting an acrylate composition with a \*\*\*thiol\*\*\* -containing ester composition and/or a hydroxy \*\*\*thiol\*\*\* -containing ester composition, both of which are described herein.

DETD The feedstock \*\*\*thiol\*\*\* ester compositions and/or hydroxy \*\*\*thiol\*\*\* ester compositions can comprise a mixture of molecules that have an average quantity of ester groups, \*\*\*thiol\*\*\* groups, hydroxy groups, and other groups and molar ratios described herein.

Additionally, individual \*\*\*thiol\*\*\* and hydroxy group reactivity within the \*\*\*thiol\*\*\* -containing ester compositions and/or hydroxy \*\*\*thiol\*\*\* ester compositions and statistical probability dictate that each thioacrylate ester molecule of the thioacrylate ester composition produced may not have the same number of ester groups, thioacrylate groups, acrylate groups, and other herein disclosed quantities of functional groups, moieties, and molar ratios.

Thus, many of the properties of the thioacrylate ester molecules within the

thioacrylate ester composition are described as using an average number of the groups per thioacrylate ester molecule within the thioacrylate ester composition or as an average ratio per thioacrylate ester molecule within the thioacrylate ester composition.

DETD The thioacrylate ester can also be described as a product produced by the process that includes contacting a \*\*\*thiol\*\*\* -containing ester composition with an acrylate composition and can be further limited by the process described herein. In other embodiments, the thioacrylate ester composition can also be described as a product produced by a process that includes contacting a hydroxy \*\*\*thiol\*\*\* -containing ester composition with an acrylate composition and can be further limited by the process described herein.

DETD The present invention advantageously provides a sulfonic acid-containing ester as an embodiment of the present invention. Generally, the sulfonic acid-containing ester of the present invention includes sulfonic acid-containing ester molecules having at least one ester group and a least one sulfonic acid group. The sulfonic acid-containing ester described herein can be produced by contacting a \*\*\*thiol\*\*\* ester with an oxidizing agent as described herein. Because the feedstock for the production of the sulfonic acid-containing ester can include multiple \*\*\*thiols\*\*\* groups, \*\*\*thiol\*\*\* group reactivity and statistical probability dictate that each sulfonic acid-containing ester molecule of the sulfonic acid-containing ester will not have the same number of sulfonic acid groups.

Additionally, the feedstock \*\*\*thiol\*\*\* ester can also include a mixture of individual \*\*\*thiol\*\*\* ester molecules having different numbers of \*\*\*thiol\*\*\* groups and/or ester groups. Thus, many of the groups present in the sulfonic acid-containing ester are described herein as an average number of the groups per sulfonic acid-containing ester molecule or an average ratio per sulfonic acid-containing ester molecule within the sulfonic acid-containing ester.

DETD In some embodiments of the present invention, the sulfonic acid ester is substantially free of \*\*\*thiol\*\*\* groups.

DETD The sulfonic acid-containing ester can also be described as a product produced by the process comprising contacting a \*\*\*thiol\*\*\*

ester with an oxidizing agent described herein.

DETD Process for Making a \*\*\*Thiol\*\*\* Ester Composition

DETD The present invention advantageously provides processes for producing a \*\*\*thiol\*\*\* ester composition as embodiments of the present invention.

As an embodiment, the present invention advantageously includes a process to produce a \*\*\*thiol\*\*\* ester composition by contacting hydrogen sulfide and an unsaturated ester composition containing unsaturated esters and reacting the hydrogen sulfide and unsaturated esters to form or produce the \*\*\*thiol\*\*\* ester composition.

As another embodiment of the present invention, a process to produce the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, the process includes contacting a composition comprising a polyol with a composition comprising a \*\*\*thiol\*\*\* containing carboxylic acid composition and reacting the polyol and \*\*\*thiol\*\*\* containing carboxylic acid composition to form the \*\*\*thiol\*\*\* ester composition.

DETD In some embodiments of the present invention that include producing \*\*\*thiol\*\*\* ester compositions, the unsaturated ester composition is a natural source oil. In an aspect, the unsaturated ester composition is soybean oil or alternatively castor oil. Other suitable types of unsaturated ester compositions are described herein and can be used in the processes for producing the \*\*\*thiol\*\*\* ester compositions.

DETD \*\*\*Thiol\*\*\* Esters from Unsaturated Esters

DETD As an embodiment of the present invention, the \*\*\*thiol\*\*\* esters described herein can be produced by a process comprising contacting hydrogen sulfide and an unsaturated ester composition and reacting hydrogen sulfide and the unsaturated ester composition to form the \*\*\*thiol\*\*\* ester composition. In one embodiment, the unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups and an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. In this embodiment, the \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules having a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

DETD The processes for producing the \*\*\*thiol\*\*\* ester composition can be applied to any of the unsaturated esters described herein and used to produce any of the \*\*\*thiol\*\*\* esters described herein. The process for producing the \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process conditions described herein.

DETD The hydrogen sulfide to molar equivalents of unsaturated ester carbon-carbon double bonds molar ratio utilized in the process to produce the \*\*\*thiol\*\*\* ester composition can be any molar ratio that produces the desired \*\*\*thiol\*\*\* ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation: 
$$\# \text{EQU} = \frac{\text{UES GMW}}{\text{UES Mass} \times \text{UES C.dbd.C}}$$
 In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the feedstock unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen sulfide to the unsaturated ester carbon-carbon double bonds of greater than 2. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio can be from 2 to 500; alternatively, from 5 to 200; alternatively, from 10 to 100; or alternatively, from 100 to 200.

DETD When a continuous reactor is used, a feed unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired \*\*\*thiol\*\*\* ester. Alternatively, the feed unsaturated ester weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed unsaturated ester weight hourly space velocity is 0.1; alternatively, the feed unsaturated ester weight hourly space velocity is 0.25; or alternatively, the feed unsaturated ester weight hourly space velocity is 2.

DETD The time required for the reaction of the unsaturated ester and hydrogen sulfide can be any time required to form the described \*\*\*thiol\*\*\* ester. Generally, the time required for the reaction of the unsaturated ester and hydrogen sulfide is at least 5 minutes.

In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In embodiments, the process to produce the \*\*\*thiol\*\*\* ester further comprises a step to remove excess or residual hydrogen sulfide after reacting the hydrogen sulfide and the unsaturated ester composition. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 0.05 weight percent sulfur; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the unsaturated ester and hydrogen sulfide can be performed at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than -20.degree. C. In other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature from -20.degree. C. to 200.degree. C.; alternatively, from 120.degree. C. to 240.degree. C.; alternatively, from 170.degree. C. to 210.degree. C.; alternatively, from 185.degree. C.



C. to 195.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD       \*\*\*Thiol\*\*\* esters having a low cyclic sulfide content can be produced using the disclosed process. In an aspect, the process for producing the \*\*\*thiol\*\*\* ester forms or produces a \*\*\*thiol\*\*\* ester having a molar ratio of cyclic sulfide to \*\*\*thiol\*\*\* groups of less than 1.5. Additional cyclic sulfide to \*\*\*thiol\*\*\* groups molar ratios are disclosed herein.

DETD       In addition to lower cyclic sulfide content, \*\*\*thiol\*\*\* esters having a low carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio can also be produced using the disclosed process. In an aspect, the process described herein produces the \*\*\*thiol\*\*\* ester having a carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio of less than 1.5. Additional carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratios are disclosed herein.

DETD       In some aspects, the process described herein produces the \*\*\*thiol\*\*\* ester molecules having an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. Additional \*\*\*thiol\*\*\* sulfur contents are disclosed herein. In other aspects, the process for producing a \*\*\*thiol\*\*\* ester forms a \*\*\*thiol\*\*\* ester having greater than 40 percent of the \*\*\*thiol\*\*\* ester total side chains include sulfur. Other percentages of the \*\*\*thiol\*\*\* ester total side chains that include sulfur are disclosed herein.

DETD       In some embodiments, the process for producing a \*\*\*thiol\*\*\* ester composition includes contacting an unsaturated ester and hydrogen sulfide and reacting the unsaturated ester and the hydrogen sulfide to form a \*\*\*thiol\*\*\* ester. The \*\*\*thiol\*\*\* ester comprises \*\*\*thiol\*\*\* ester molecules that have a ratio of cyclic sulfide to \*\*\*thiol\*\*\* groups of less than 1.5.

DETD       Tool Ester from a Polyol and a \*\*\*Thiol\*\*\* Containing Carboxylic Acid Derivative

DETD       As another embodiment of the present invention, another process to produce the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the

polyol and \*\*\*thiol\*\*\* containing carboxylic acid and/or  
\*\*\*thiol\*\*\* containing carboxylic acid derivative to produce  
the \*\*\*thiol\*\*\* ester composition. This process can be applied to  
any polyol, \*\*\*thiol\*\*\* containing carboxylic acid, or  
\*\*\*thiol\*\*\* containing carboxylic acid derivative described herein. The  
process for producing the \*\*\*thiol\*\*\* ester composition can also include  
any additional process steps or process conditions described herein.  
Additionally, the process for producing the \*\*\*thiol\*\*\* ester  
composition can form any \*\*\*thiol\*\*\* ester described herein.  
DETD In some embodiments, the \*\*\*thiol\*\*\* ester composition  
includes \*\*\*thiol\*\*\* ester molecules that have an average of at least  
1.5 ester groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups per  
\*\*\*thiol\*\*\* ester molecule.  
DETD The polyol used to produce the \*\*\*thiol\*\*\* ester by  
contacting a polyol and a \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\*  
carboxylic acid equivalent (for example a \*\*\*thiol\*\*\*  
carboxylic acid methyl ester) can be any polyol or mixture of polyols that  
can produce the described \*\*\*thiol\*\*\* containing ester.  
DETD In one aspect, the polyol used to produce the \*\*\*thiol\*\*\*  
ester can comprise from 2 to 20 carbon atoms. In other embodiments, the  
polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7  
carbon atoms; alternatively from 2 to 5 carbon atoms. In further  
embodiments, the polyol may be a mixture of polyols having an average of 2 to  
20 carbon atoms; alternatively, an average of from 2 to 10 carbon  
atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively  
an average of 2 to 5 carbon atoms.  
DETD In another aspect, the polyol used to produce the \*\*\*thiol\*\*\*  
ester can have any number of hydroxy groups needed to produce the  
\*\*\*thiol\*\*\* ester as described herein. In some embodiments,  
the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups;  
alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or  
alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at  
least 2 hydroxy groups; alternatively at least 3 hydroxy groups;  
alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy  
groups;  
at least 6 hydroxy groups. In yet other embodiments, the polyol  
comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4

hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the \*\*\*thiol\*\*\* ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the \*\*\*thiol\*\*\* ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\* ester by contacting a polyol and a \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent can be any \*\*\*thiol\*\*\* carboxylic acid mixture comprising \*\*\*thiol\*\*\* carboxylic acids, \*\*\*thiol\*\*\* carboxylic acid equivalent or mixture comprising \*\*\*thiol\*\*\* carboxylic acid equivalents that can produce the described \*\*\*thiol\*\*\* containing ester. When talking about the characteristics \*\*\*thiol\*\*\* carboxylic acid equivalent or \*\*\*thiol\*\*\* carboxylic acid equivalents, properties such as number of carbon atoms, average number of carbon atom, molecular weight or average molecular weight, number of

groups, one **\*\*\*thiol\*\*\*** group, and average number of **\*\*\*thiol\*\*\***  
 will understand the these properties will apply to the portion of  
 the **\*\*\*thiol\*\*\*** carboxylic acid equivalent which adds to the  
 polyol to form the **\*\*\*thiol\*\*\*** ester.  
 DETD In an aspect, the **\*\*\*thiol\*\*\*** carboxylic acid and/or  
**\*\*\*thiol\*\*\*** carboxylic acid equivalent used to produce the **\*\*\*thiol\*\*\***  
 ester comprises from 2 to 28 carbon atoms. In an embodiment, the  
**\*\*\*thiol\*\*\*** carboxylic acid and/or **\*\*\*thiol\*\*\*** carboxylic acid equivalent  
 comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24  
 carbon atoms; alternatively, from 12 to 24 carbon atoms; or  
 alternatively, from 14 to 20 carbon atoms. In other embodiments, a mixture comprising  
**\*\*\*thiol\*\*\*** carboxylic acid and/or mixture comprising  
**\*\*\*thiol\*\*\*** carboxylic acid equivalents has an average of 2 to 28 carbon  
 atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively,  
 from 4 to 26 carbon atoms per carboxylic acid and/or carboxylic acid  
 equivalent; alternatively, from 8 to 24 carbon atoms per  
 carboxylic acid and/or carboxylic acid equivalent; alternatively, from 12 to 24  
 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; or  
 alternatively, from 14 to 20 carbon atoms per carboxylic acid  
 and/or carboxylic acid equivalent.  
 DETD In another aspect, the **\*\*\*thiol\*\*\*** carboxylic acid and/or  
**\*\*\*thiol\*\*\*** carboxylic acid equivalent used to produce the  
**\*\*\*thiol\*\*\*** ester has at least 1 **\*\*\*thiol\*\*\*** group;  
 alternatively 2 **\*\*\*thiol\*\*\*** groups. In some embodiments, a mixture  
 comprising **\*\*\*thiol\*\*\*** carboxylic acid and/or mixture comprising  
**\*\*\*thiol\*\*\*** carboxylic acid equivalents has an average of from 0.5 to 3  
**\*\*\*thiol\*\*\*** groups per carboxylic acid and/or carboxylic acid  
 equivalent; alternatively, an average of from 1 to 2  
**\*\*\*thiol\*\*\*** groups per carboxylic acid and/or carboxylic acid equivalent.  
 DETD In another aspect, the **\*\*\*thiol\*\*\*** carboxylic acid and/or  
**\*\*\*thiol\*\*\*** carboxylic acid equivalent used to produce the  
**\*\*\*thiol\*\*\*** ester has a molecular weight greater than 100;  
 alternatively greater than 180; alternatively greater than 240;  
 or alternatively greater than 260. In other embodiments, the  
**\*\*\*thiol\*\*\*** carboxylic acid and/or **\*\*\*thiol\*\*\*** carboxylic acid equivalent  
 has a molecular weight from 100 to 500; alternatively, from 120 to 420;  
 alternatively, from 180 to 420; alternatively, from 240 to 420; a  
 mixture or alternatively, from 260 to 360. In some embodiments, a  
 mixture comprising **\*\*\*thiol\*\*\*** carboxylic acid and/or mixture

comprising \*\*\*thiol\*\*\* carboxylic acid equivalents has an average molecular weight greater than 100 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 180 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 240 per carboxylic acid and/or carboxylic acid equivalent; or alternatively greater than 260 per carboxylic acid and/or carboxylic acid equivalent.

In yet other embodiments, the mixture comprising of \*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising \*\*\*thiol\*\*\* carboxylic acid equivalents has an average molecular weight from 100 to 500 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 180 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 240 to 420 per carboxylic acid and/or carboxylic acid equivalent; a mixture or alternatively, from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.

DETD In some aspects, the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the presence of a solvent. In other aspects the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof.

Generally, the solvent, regardless of its chemical class, can include from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl

ether,  
dipropyl ether, tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and the

\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the

\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester oil; alternatively, less than 15 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 10 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the

\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the

\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the

\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, from 5 times to 10 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD The equivalent of \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the \*\*\*thiol\*\*\* ester composition can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired \*\*\*thiol\*\*\* ester composition. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater

than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio can range from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid.

Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree. C. In other embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree. C.

DETD The time required for the reaction of the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative is catalyzed.

acid derivative can be any time required to form the described  
\*\*\*thiol\*\*\* ester oil. Generally, the reaction time of the  
polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or  
\*\*\*thiol\*\*\* containing carboxylic acid derivative is at least 5 minutes. In  
some embodiments, the reaction time is at least 30 minutes;  
alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other  
embodiments, the reaction time ranges from 5 minutes to 72 hours;  
alternatively, from 30 minutes to 48 hours; alternatively, from 1  
hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.  
DETD When a continuous reactor is used, a feed polyol weight  
unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be  
used to produce the desired \*\*\*thiol\*\*\* ester. Alternatively, the  
feed polyol weight hourly space velocity ranges between 0.1 to 5;  
alternatively, from 0.1 to 2. Alternatively, the feed polyol  
ester weight hourly space velocity is 0.1; alternatively, the feed  
polyol weight hourly space velocity is 0.25; or alternatively, the feed  
polyol weight hourly space velocity is 2.  
DETD The reaction between the polyol and the \*\*\*thiol\*\*\*  
containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid  
derivative can be performed at any reaction pressure that  
maintains the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or  
\*\*\*thiol\*\*\* containing carboxylic acid derivative in a liquid  
state. In some embodiments, the reaction between the polyol and the  
\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\*  
containing carboxylic acid derivative is performed at a pressure  
ranging from 0 psia to 2000 psia. In other embodiments, the reaction  
pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and  
500 psia; or alternatively, 0 psia to 300 psia.  
DETD In some embodiments, the process to produce the \*\*\*thiol\*\*\*  
ester by reacting a polyol and the \*\*\*thiol\*\*\* containing  
carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can  
further include a step to remove excess or residual polyol, \*\*\*thiol\*\*\*  
containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing  
carboxylic acid derivative once the polyol has reacted with the  
\*\*\*thiol\*\*\* containing carboxylic acid or \*\*\*thiol\*\*\* containing  
carboxylic acid derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is  
vacuum



stripped. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 5 excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 2 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 1 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD Process for Making Hydroxy \*\*\*Thiol\*\*\* Ester Composition

DETD The present invention advantageously provides processes for producing a hydroxy \*\*\*thiol\*\*\* ester as embodiments of the present invention.

As an embodiment, the present invention includes a process to produce the hydroxy \*\*\*thiol\*\*\* ester. The process comprises the steps of contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to form the hydroxy \*\*\*thiol\*\*\* ester. As another embodiment of the present invention, another process to produce the hydroxy \*\*\*thiol\*\*\* ester is provided. In this embodiment, the process comprises the steps of contacting a composition comprising a polyol with a composition comprising an hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or an hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or the hydroxy

\*\*\*thiol\*\*\*  
 containing carboxylic acid derivative to form the hydroxy  
 \*\*\*thiol\*\*\*  
 ester.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester from Hydrogen Sulfide and an  
 Epoxidized  
 Unsaturated Ester Composition

DETD As an embodiment of the present invention, the hydroxy  
 \*\*\*thiol\*\*\*  
 ester composition is produced by a process comprising the steps  
 of  
 contacting hydrogen sulfide and an epoxidized unsaturated ester  
 composition and reacting the hydrogen sulfide and the epoxidized  
 unsaturated ester to produce the hydroxy \*\*\*thiol\*\*\* ester  
 composition.

DETD In some embodiments, the epoxidized unsaturated ester  
 composition  
 includes epoxidized unsaturated esters that have an average of at  
 least  
 1 ester groups and an average of at least 1 \*\*\*epoxide\*\*\*  
 groups per  
 epoxidized unsaturated ester molecule.

DETD The process for producing or preparing the hydroxy \*\*\*thiol\*\*\*  
 ester composition can be applied to any of the epoxidized  
 unsaturated  
 esters described herein and used to produce any hydroxy  
 \*\*\*thiol\*\*\*  
 ester described herein. The process for producing the hydroxy  
 \*\*\*thiol\*\*\* ester can also include any additional process  
 steps or  
 process conditions as described herein. Additionally, the process  
 for  
 producing the hydroxy \*\*\*thiol\*\*\* ester can form any hydroxy  
 \*\*\*thiol\*\*\* ester described herein.

DETD In some aspects, the hydroxy \*\*\*thiol\*\*\* ester is produced  
 by  
 contacting hydrogen sulfide with the epoxidized natural source  
 oil under  
 the reaction conditions to form the hydroxy \*\*\*thiol\*\*\* ester  
 in the  
 presence of an optional catalyst. In some embodiments, the  
 catalyst can  
 be a heterogeneous catalyst or a homogeneous catalyst. Examples  
 of  
 suitable catalysts are described herein. Additional types of  
 suitable  
 catalysts will be apparent to those of skill in the art and are  
 to be  
 considered within the scope of the present invention.

DETD The hydrogen sulfide to molar equivalents of \*\*\*epoxide\*\*\*  
 groups  
 in the epoxidized unsaturated ester (hereinafter "hydrogen  
 sulfide to  
 \*\*\*epoxide\*\*\* group molar ratio") utilized in the process to  
 produce  
 the hydroxy \*\*\*thiol\*\*\* ester can be any hydrogen sulfide to  
 \*\*\*epoxide\*\*\* group molar ratio that produces the desired  
 hydroxy  
 \*\*\*thiol\*\*\* ester. The molar equivalents of epoxidized  
 unsaturated

ester epoxidized groups can be calculated by the equation:  
##EQU2##  
In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES \*\*\*Epoxide\*\*\* is the average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio ranges from 0.2 to 5; alternatively, from 0.5 to 4; or alternatively, from 0.75 to 3. In some embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio can be from 0.2 to 500; alternatively, from 0.5 to 400; alternatively, from 1 to 300; alternatively, from 2 to 250; alternatively, 5 to 200; or alternatively, from 10 to 100.

DETD The time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide can be any time required to form the described hydroxy \*\*\*thiol\*\*\* ester. Generally, the time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide is at least 15 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of greater than 2.5 weight percent \*\*\*thiol\*\*\* sulfur. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. Alternatively, in some

embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

DETD In other aspects, the process producing the hydroxy \*\*\*thiol\*\*\* ester composition includes producing hydroxy \*\*\*thiol\*\*\* ester molecules having an average of greater than 40 percent of the sulfide-containing ester total side chains comprise a sulfide group.

Additional embodiments wherein the hydroxy \*\*\*thiol\*\*\* ester comprises a percentage of sulfide-containing ester total side chains are described herein.

DETD In embodiments, the process to produce the hydroxy \*\*\*thiol\*\*\* ester further comprises a step to remove residual hydrogen sulfide after reacting the hydrogen sulfide and the epoxidized unsaturated ester composition. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the hydrogen sulfide and the epoxidized unsaturated ester can be performed at any temperature capable of forming the hydroxy \*\*\*thiol\*\*\* ester. In some embodiments, the epoxidized unsaturated ester and hydrogen sulfide can be reacted at a reaction temperature greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments,

the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD In another aspect, the process to produce a hydroxy \*\*\*thiol\*\*\* ester produces a hydroxy \*\*\*thiol\*\*\* ester having an \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio less than 3.3. In another aspect, the process to produce a hydroxy \*\*\*thiol\*\*\* ester produces a hydroxy \*\*\*thiol\*\*\* ester having an \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio less than 2. Other hydroxy ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratios are described herein. Alternatively, the hydroxy \*\*\*thiol\*\*\* ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1.

In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester can be substantially free of \*\*\*epoxide\*\*\* groups.

DETD In another aspect, the process to produce hydroxy \*\*\*thiol\*\*\* ester produces a hydroxy \*\*\*thiol\*\*\* ester wherein at least 20 percent of the side chains comprise an .alpha.-hydroxy \*\*\*thiol\*\*\* group. Other hydroxy \*\*\*thiol\*\*\* ester embodiments wherein the hydroxy \*\*\*thiol\*\*\* ester contains a percentage of side chains comprising .alpha.-hydroxy \*\*\*thiol\*\*\* groups are described herein.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester from a Polyol and a Hydroxy \*\*\*Thiol\*\*\* Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to prepare the hydroxy \*\*\*thiol\*\*\* ester is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid to form a hydroxy \*\*\*thiol\*\*\* ester composition. This process can be applied to any polyol, any hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, or any \*\*\*thiol\*\*\* containing carboxylic acid derivative described herein. The process for

producing the hydroxy \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the hydroxy \*\*\*thiol\*\*\* ester composition can form any \*\*\*thiol\*\*\* ester described herein.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD The polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester by contacting a polyol and a hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent (for example a hydroxy \*\*\*thiol\*\*\* carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described \*\*\*thiol\*\*\* containing ester.

DETD In one aspect, the polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester can have any number of hydroxy groups needed to produce the hydroxy \*\*\*thiol\*\*\* ester as described herein. In some embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester is a mixture of polyols. In an embodiment, the

mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the hydroxy \*\*\*thiol\*\*\* ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the hydroxy \*\*\*thiol\*\*\* ester by contacting a polyol and a hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent can be any hydroxy \*\*\*thiol\*\*\* carboxylic acid mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids, hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents that can produce the described hydroxy \*\*\*thiol\*\*\* containing ester. When talking about the characteristics hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents, properties such as number of carbon atoms, average number of carbon atom, molecular weight or average molecular weight, number of \*\*\*thiol\*\*\* group, and average number of \*\*\*thiol\*\*\* groups, one will understand the these properties will apply to the portion of the \*\*\*thiol\*\*\* carboxylic

acid equivalent which adds to the polyol to form the  
 \*\*\*thiol\*\*\*  
 ester.  
 DETD In an aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or  
 hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to  
 produce the  
 \*\*\*thiol\*\*\* ester comprises from 2 to 28 carbon atoms. In an  
 embodiment, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or  
 hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents comprises from 4 to  
 26 carbon  
 atoms; alternatively, from 8 to 24 carbon atoms; alternatively,  
 from 12  
 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms.  
 In  
 other embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\*  
 carboxylic acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\*  
 carboxylic acid equivalents has an average of 2 to 28 carbon  
 atoms per  
 carboxylic acid and/or carboxylic acid equivalent; alternatively,  
 from 4  
 to 26 carbon per carboxylic acid and/or carboxylic acid  
 equivalent;  
 alternatively, from 8 to 24 carbon atoms per carboxylic acid  
 and/or  
 carboxylic acid equivalent; alternatively, from 12 to 24 carbon  
 atoms  
 per carboxylic acid and/or carboxylic acid equivalent; or  
 alternatively,  
 from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic  
 acid  
 equivalent.  
 DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid  
 and/or  
 hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to  
 produce the  
 \*\*\*thiol\*\*\* ester has at least 1 \*\*\*thiol\*\*\* group;  
 alternatively  
 2 \*\*\*thiol\*\*\* groups. In some embodiments, a mixture  
 comprising  
 hydroxy \*\*\*thiol\*\*\* carboxylic acids and/or mixture  
 comprising  
 hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an  
 average of  
 from 0.5 to 3 \*\*\*thiol\*\*\* groups per carboxylic acid and/or  
 carboxylic acid equivalent; alternatively, an average of from 1  
 to 2  
 \*\*\*thiol\*\*\* groups per carboxylic acid and/or carboxylic acid  
 equivalent.  
 DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid  
 and/or  
 hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to  
 produce the  
 \*\*\*thiol\*\*\* ester has at least 1 hydroxy group;  
 alternatively, at  
 least 2 hydroxy groups. In some embodiments, a mixture comprising  
 hydroxy \*\*\*thiol\*\*\*  
 carboxylic acids and/or mixture  
 comprising  
 hydroxy \*\*\*thiol\*\*\*  
 carboxylic acid equivalents has an  
 average of



from 0.5 to 3 hydroxy groups per carboxylic acid and/or  
 carboxylic acid  
 equivalent; alternatively, an average of from 1 to 2 hydroxy  
 groups per  
 carboxylic acid and/or carboxylic acid equivalent.  
 DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid  
 and/or  
 hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to  
 produce the  
 hydroxy \*\*\*thiol\*\*\* ester has a molecular weight greater than  
 100;  
 alternatively greater than 180; alternatively greater than 240;  
 or  
 alternatively greater than 260. In other embodiments, the hydroxy  
 \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\*  
 carboxylic  
 acid equivalent has a molecular weight from 100 to 500;  
 alternatively,  
 from 120 to 420; alternatively, from 180 to 420; alternatively,  
 from 240  
 to 420; a mixture or alternatively, from 260 to 360. In some  
 embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\*  
 carboxylic  
 acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\*  
 carboxylic acid  
 equivalents has an average molecular weight greater than 100 per  
 carboxylic acid and/or carboxylic acid equivalent; alternatively  
 greater  
 than 180 per carboxylic acid and/or carboxylic acid equivalent;  
 alternatively greater than 240 per carboxylic acid and/or  
 carboxylic  
 acid equivalent; or alternatively greater than 260 per carboxylic  
 acid  
 and/or carboxylic acid equivalent. In yet other embodiments, the  
 mixture  
 comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or mixture  
 comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents  
 has an  
 average molecular weight from 100 to 500 per carboxylic acid  
 and/or  
 carboxylic acid equivalent; alternatively, from 120 to 420 per  
 carboxylic acid and/or carboxylic acid equivalent; alternatively,  
 from  
 180 to 420 per carboxylic acid and/or carboxylic acid equivalent;  
 alternatively, from 240 to 420 per carboxylic acid and/or  
 carboxylic  
 acid equivalent; a mixture or alternatively, from 260 to 360 per  
 carboxylic acid and/or carboxylic acid equivalent.  
 DETD In some aspects, the reaction between the polyol and the hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid derivative occurs in the presence of a  
 solvent. In other aspects, the reaction between the polyol and  
 the  
 hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in  
 the  
 substantial absence of a solvent. In aspects wherein the reaction  
 between the polyol and the hydroxy \*\*\*thiol\*\*\* containing  
 carboxylic

acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the hydroxy \*\*\*thiol\*\*\* ester; alternatively, less than 15 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 10 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, from 5 times to 10 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative.

acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD The equivalents of hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter referred to as "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the hydroxy \*\*\*thiol\*\*\* ester can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired hydroxy \*\*\*thiol\*\*\* ester. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio ranges from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid. Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any temperature capable of forming the hydroxy \*\*\*thiol\*\*\* ester.

In some embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid

acid derivative can be reacted at a temperature greater than 20.degree.

C. In other embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree..

DETD The time required for the reaction of the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be any time required to form the described hydroxy \*\*\*thiol\*\*\* ester composition.

Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD The reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative in a liquid state. In some embodiments, the reaction pressure ranges from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500 psia; or alternatively, from 0 psia to 300 psia.

DETD In some embodiments, the process to produce the hydroxy \*\*\*thiol\*\*\* ester composition by reacting a polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can further include a step to remove excess

acid, or residual polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic  
and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid  
derivative  
once the polyol has reacted with the hydroxy \*\*\*thiol\*\*\*  
containing  
carboxylic acid or hydroxy \*\*\*thiol\*\*\* containing carboxylic  
acid  
derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is  
vacuum  
stripped. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester  
is  
vacuum stripped at a temperature between 25.degree. C. and  
250.degree.  
C.; or alternatively, between 50.degree. C. and 200.degree. C. In  
other  
embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an  
inert  
gas to remove excess polyol, hydroxy \*\*\*thiol\*\*\* containing  
carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing  
carboxylic  
acid derivative. In some embodiments, the hydroxy \*\*\*thiol\*\*\*  
ester  
is sparged with an inert gas at a temperature between 25.degree.  
C. and  
250.degree. C., or alternatively, between 50.degree. C. and  
200.degree.  
C. In some aspects, the inert gas is nitrogen. Generally, the  
stripped  
or sparged hydroxy \*\*\*thiol\*\*\* ester oil comprises less than  
5  
excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic  
acid, or  
hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In  
other  
embodiments, the stripped or sparged hydroxy \*\*\*thiol\*\*\*  
ester oil  
comprises less than 2 weight percent excess polyol, hydroxy  
\*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy  
\*\*\*thiol\*\*\*  
containing carboxylic acid derivative; less than 1 weight percent  
excess  
polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid,  
and/or  
hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or  
alternatively, less than 0.5 weight percent excess polyol,  
hydroxy  
\*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy  
\*\*\*thiol\*\*\*  
containing carboxylic acid derivative.  
DETD A method of making a thioacrylate containing ester composition  
is  
advantageously provided as another embodiment of the present  
invention.  
The process for producing the thioacrylate containing ester  
comprising  
contacting a \*\*\*thiol\*\*\* ester with an acrylate and  
converting at  
least one \*\*\*thiol\*\*\* group to a \*\*\*thiol\*\*\* acrylate  
group. The

process can be applied to any of the \*\*\*thiol\*\*\* esters described herein and used to any thioacrylate ester described herein. The process for producing the thioacrylate ester can also include any additional process steps or process conditions described herein.

DETD The acrylate compound can be any acrylate compound capable of reacting with a \*\*\*thiol\*\*\* group to form the \*\*\*thiol\*\*\* acrylate group.

In some embodiments, the acrylate compound can be an acrylic halide. In other embodiments, the acrylate compound can be an acrylic acid. In yet other embodiments, the acrylate compound can be an acrylic anhydride.

DETD In some aspects, the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the presence of a solvent. In other aspects the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the substantial absence of a solvent. In aspects wherein the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the presence of a solvent, the solvent may be an aliphatic hydrocarbon, an ether, and aromatic compound. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof.

When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the \*\*\*thiol\*\*\* ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, less than 15 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, less than 10 times the mass of the \*\*\*thiol\*\*\* ester; or alternatively, less than 5 times the mass

of the \*\*\*thiol\*\*\* ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, from 3 times to 15 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, 4 times to 15 times the mass of the \*\*\*thiol\*\*\* ester; or alternatively, from 5 times to 10 times the mass of the \*\*\*thiol\*\*\* ester.

DETD In some aspects the conversion of the \*\*\*thiol\*\*\* group to the thioacrylate group occurs in the presence of a catalyst. In some embodiments, the catalyst is homogeneous. In some embodiments, the catalyst is an organic amine. Examples of suitable organic amines include triethylamine, tripropylamine, tributylamine, and pyridine. In other embodiments, the catalyst is heterogeneous. Examples of suitable catalysts include Amberlyst A-21 and Amberlyst A-26. Other suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group can be performed at any conversion temperature that is capable of converting the \*\*\*thiol\*\*\* group to a thioacrylate group. In some embodiments, the conversion temperature is greater than -20.degree. C. In other embodiments, the conversion temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the conversion temperature ranges from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 50.degree. C. to 150.degree. C.

DETD The conversion time required for the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group can be any time required to form the described thioacrylate containing ester. Generally, the conversion time is at least 5 minutes. In some embodiments, the conversion time is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In other embodiments, the conversion time ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; or alternatively, from 45 minutes to 3 hours.

DETD The conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group can be performed at any conversion pressure that maintains the \*\*\*thiol\*\*\* ester and the acrylate compound in the liquid state. In some embodiments, the conversion pressure ranges from 0 psia to 2000 psia. In other embodiments, the conversion pressure ranges from 0 psia to 1000 psia; or alternatively, from 0 psia to 500 psia.

DETD Process for Producing Cross-Linked \*\*\*Thiol\*\*\* Ester

DETD As an embodiment of the present invention, a process for producing a cross-linked \*\*\*thiol\*\*\* ester composition is advantageously provided. Minimally, in some embodiments, the process to produce the cross-linked \*\*\*thiol\*\*\* ester composition comprises contacting a \*\*\*thiol\*\*\* ester composition with an oxidizing agent and reacting the \*\*\*thiol\*\*\* ester composition and an oxidizing agent to form the \*\*\*thiol\*\*\* ester oligomer having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having the structure -S.sub.Q-, wherein Q is an integer greater than 1. The disclosed method may be applied to any \*\*\*thiol\*\*\* ester described herein to produce any cross-linked \*\*\*thiol\*\*\* ester composition as described herein.

process The process to produce the cross-linked \*\*\*thiol\*\*\* ester composition can also include any additional process steps or conditions as described herein.

DETD When elemental sulfur is used as the oxidizing agent, the quantity of elemental sulfur utilized to form the cross-linked \*\*\*thiol\*\*\* ester composition is determined as a function of the \*\*\*thiol\*\*\* sulfur content of the \*\*\*thiol\*\*\* ester composition. In an aspect, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition is at least 0.5. In some embodiments, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition is at least 5; alternatively, at least 10, alternatively, at least 15, or alternatively, at least 20. In other embodiments, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition ranges from 0.5 to 32; alternatively, ranges from 1 to 24; alternatively, ranges from 2 to 16; or alternatively, ranges from 3 to 10.

DETD In an aspect, the reaction of the \*\*\*thiol\*\*\* ester and



elemental sulfur occurs in the presence of a catalyst. The catalyst can be any catalyst that catalyzes the formation of the polysulfide linkage between at least two \*\*\*thiol\*\*\* ester monomers. In some embodiments, the catalyst is an amine. In further embodiments, the catalyst is a tertiary amine.

DETD The formation of the cross-linked \*\*\*thiol\*\*\* ester can occur in a batch reactor or a continuous reactor, as described herein. The formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at a temperature greater than 25.degree. C. In other embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at a temperature greater than 50.degree. C.; alternatively, greater than 70.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester occurs at a temperature from 25.degree. C. to 150.degree. C.; alternatively, from 50.degree. C. to 150.degree. C.; alternatively, from 70.degree. C. to 120.degree. C.; or alternatively, from 80.degree. C. to 110.degree. C.

DETD The time required to form the cross-linked \*\*\*thiol\*\*\* ester can be any time required to form the desired cross-linked \*\*\*thiol\*\*\* ester. Generally, the time required to form the cross-linked \*\*\*thiol\*\*\* ester is at least 15 minutes. In some embodiments, the time required to form the cross-linked \*\*\*thiol\*\*\* ester is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the time required to form the cross-linked \*\*\*thiol\*\*\* ester ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD In embodiments, the process to produce the cross-linked \*\*\*thiol\*\*\* ester further comprises a step to remove residual hydrogen sulfide. In some embodiments the cross-linked \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester is vacuum striped at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or

alternatively, 75 and 150.degree. C. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester oil is sparged with an inert gas to remove residual hydrogen sulfide. In other embodiments, the cross-linked \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, between 75 and 150.degree. C. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked \*\*\*thiol\*\*\* ester with an inert gas. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked \*\*\*thiol\*\*\* ester an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the inert gas is nitrogen.

DETD Generally, the stripped or sparged cross-linked \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* -containing ester oil comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The present invention advantageously provides processes for producing sulfide-containing esters as embodiments of the present invention. Generally, the sulfide-containing esters can be prepared by two processes. As an embodiment of the present invention, the first process used to produce a sulfide-containing ester comprises contacting an unsaturated ester and a \*\*\*mercaptan\*\*\* and reacting the unsaturated ester and \*\*\*mercaptan\*\*\* to form a sulfide-containing ester.

As another embodiment of the present invention, the second process used to produce a sulfide-containing ester comprises contacting an epoxidized unsaturated ester and a \*\*\*mercaptan\*\*\* sulfide and reacting the unsaturated ester and \*\*\*mercaptan\*\*\* to form a sulfide-containing ester. Additional aspects of the two sulfide-containing ester production processes are described below.

DETD The sulfide-containing esters and sulfide-containing ester compositions described herein can be produced by a process comprising contacting a \*\*\*mercaptan\*\*\* and an unsaturated ester and reacting the

\*\*\*mercaptan\*\*\* and the unsaturated ester to form a sulfide-containing ester. The process can be applied to any of the unsaturated esters and \*\*\*mercaptans\*\*\* described herein. The process for producing the sulfide-containing ester can also include any additional process steps or process conditions described herein. Additionally, the process for producing the sulfide-containing ester can form any sulfide-containing ester described herein.

DETD In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, an alcohol, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an alcohol, the alcohol is methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester; alternatively, less than 15 times the mass of the unsaturated ester; alternatively, less than 10 times the mass of the unsaturated ester; or alternatively, less than 5 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20

times the mass of the unsaturated ester; alternatively, from 3 times to 15 times the mass of the unsaturated ester; alternatively, from 4 times to 15 times the mass of the unsaturated ester; or alternatively, from 5 times to 10 times the mass of the unsaturated ester.

DETD The molar ratio of \*\*\*mercaptan\*\*\* to molar equivalents of unsaturated ester carbon-carbon double bonds (herein after "\*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio") utilized in the process to produce the sulfide-containing ester can be any \*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio that produces the desired sulfide-containing ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation:  $\frac{UES\ C.dbd.C}{UES\ Mass}$  In this equation, UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the \*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio is greater than 0.25. In other embodiments, the \*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio is greater than 0.5; alternatively, greater than 0.75; alternatively, greater than 1; alternatively, greater than 1.25; or alternatively, greater than 1.5. In other embodiments, the \*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio can range from 0.25 to 2; alternatively, from 0.5 to 1.5, or alternatively, from 0.75 to 1.25.

DETD In some aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester is catalyzed. The reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester can be catalyzed by a heterogeneous catalyst or homogeneous catalyst, as described herein. In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by a free radical initiator or ultraviolet radiation, as described herein.

DETD The free radical initiator can be any free radical initiator capable of forming free radicals under thermal or light photolysis. Generally, the free radical initiator is selected from the general class of compounds having a --N.dbd.N-- group or a --O-- O-- group. Specific classes of free radical initiators include diazo compounds, dialkyl peroxides, hydroperoxides, and peroxy esters. Specific initiators include

azobenzene, 2,2'-azobis(2-methylpropionitrile, 4,4'-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobis(2methylpropane), 2,2'-azobis(2-methylpropionamide) dihydrochloride, methylpropionitrile, azodicarboxamide, tert-butyl hydroperoxide, di-tert-butyl peroxide, octylperbenzoate. In some embodiments, the free radical initiated reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is performed at a reaction temperature within +50.degree. C. of the 1 hour half life of the free radical initiator. In other embodiments, the reaction temperature is within +-.25.degree. C. of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within +-.20.degree. C. of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within +-.15.degree. C. of the 1 hour half life of the free radical initiator; or alternatively, the reaction temperature is within +-.10.degree. C. of the 1 hour half life of the free radical initiator. In embodiments where the free radical initiated reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by light photolysis, the light can be any light capable creating free radicals. In some embodiments, the light is UV radiation. Other sources of light capable of creating free radicals will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In another aspect, the reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by UV radiation. In these embodiments, the UV radiation may be any UV radiation capable of initiating the reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester. In some embodiments, the UV radiation is generated by a medium pressure mercury lamp.

DETD The reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester can occur in a batch reactor of a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction time for reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester can be any time required to form the sulfide-containing ester. Generally, the reaction time is at least 5

minutes. In some embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In some embodiments, the process to produce the sulfide-containing ester further comprises a step to remove any residual \*\*\*mercaptan\*\*\* that remains after reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester. In some embodiments, the sulfide-containing ester is vacuum stripped to remove the residual \*\*\*mercaptan\*\*\*. In some embodiments, the sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the sulfide-containing ester is sparged with an inert gas to remove the residual \*\*\*mercaptan\*\*\*. In some embodiments, the sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged sulfide-containing ester comprises less than 5 weight percent of the \*\*\*mercaptan\*\*\*. In other embodiments, the stripped or sparged sulfide-containing ester comprises less than 2 weight percent of the \*\*\*mercaptan\*\*\*; alternatively, less than 1 weight percent of the \*\*\*mercaptan\*\*\*; or alternatively, less than 0.5 weight percent of the \*\*\*mercaptan\*\*\*.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester can be performed at any temperature capable of forming the sulfide-containing ester. In some embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester can be reacted at a reaction temperature of greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester can be reacted at a temperature from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 80.degree. C. to 160.degree. C.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the unsaturated

ester can be performed at any pressure that maintains the  
\*\*\*mercaptan\*\*\* and the unsaturated ester in a substantially liquid state. In  
some embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester  
can be performed at a reaction pressure ranging from 0 psig to 2000  
psig. In other embodiments, the reaction pressure ranges from 0 psig to  
1000 psig; alternatively, from 0 psig to 500 psig; or alternatively,  
from 0 psig to 200 psig.  
DETD Using the disclosed process, sulfide-containing ester having a  
low carbon-carbon double bond to sulfide group molar ratio can be  
produced. In an aspect, the process for producing the sulfide-containing  
ester forms a sulfide-containing ester having a carbon-carbon double  
bond to \*\*\*thiol\*\*\* group molar ratio of less than 1.5. Additional  
carbon-carbon double bond to sulfide group molar ratios are  
disclosed herein.  
DETD As another embodiment of the present invention, another process  
for producing a class of sulfide-containing esters, which includes  
hydroxy sulfide-containing esters, is advantageously provided. In this  
embodiment, the hydroxy sulfide-containing esters and hydroxy  
sulfide-containing ester compositions can be produced by a  
process comprising the steps of contacting a \*\*\*mercaptan\*\*\* and an  
epoxidized unsaturated ester and reacting the \*\*\*mercaptan\*\*\*  
and the epoxidized unsaturated ester to produce or form the hydroxy  
sulfide-containing ester. The process can be applied to any  
\*\*\*mercaptan\*\*\* and/or any epoxidized unsaturated esters  
described herein. The process for producing the hydroxy sulfide-containing  
ester can also include any additional process steps or process  
conditions as described herein. Additionally, the process for producing the  
hydroxy sulfide-containing ester can form any hydroxy sulfide-containing  
ester as described herein.  
DETD In some aspects, the reaction between the \*\*\*mercaptan\*\*\*  
and the unsaturated ester occurs in the presence of a solvent. In other  
aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated  
ester occurs in the substantial absence of a solvent. When the reaction  
occurs in the presence of a solvent, the solvent is selected from an  
aliphatic

hydrocarbon, an ether, an aromatic compound, or any combination thereof.

Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms.

When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the epoxidized unsaturated ester; alternatively, less than 15 times the mass of the epoxidized unsaturated ester; alternatively, less than 10 times the mass of the epoxidized unsaturated ester; or alternatively, less than 5 times the mass of the epoxidized unsaturated ester.

In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the epoxidized unsaturated ester; alternatively, from 3 times to 15 times the mass of the epoxidized unsaturated ester; alternatively, from 4 times to 15 times the mass of the epoxidized unsaturated ester; or alternatively, from 5 times to 10 times the mass of the epoxidized unsaturated ester.

DETD The reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can occur using any \*\*\*mercaptan\*\*\* to molar equivalents of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester (hereinafter referred to as " \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio") that is capable of producing the herein described .alpha.-hydroxy \*\*\*thiol\*\*\* esters. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation: ##EQU4##

DETD In this equation, EUES GMW is the average gram molecular weight



of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES \*\*\*Epoxide\*\*\* is the average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.2. In other embodiments, the \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio ranges from 0.2 to 10; alternatively, from 0.5 to 8; alternatively, from 0.75 to 5; or alternatively, from 1 to 3.

DETD In some aspects, the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester to produce the desired hydroxy \*\*\*thiol\*\*\* ester. In one aspect, the catalyst is selected from the group consisting of homogeneous and heterogeneous catalysts. In other aspects, the catalyst is selected from the group consisting of zeolites, heterogeneous catalysts, homogeneous catalysts, and mixtures thereof. In another aspect, the catalyst is an amine. In other aspects, the catalyst is selected from the group consisting of cyclic conjugated amines, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and mixtures thereof.

DETD In some aspects, the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester to produce the desired hydroxy \*\*\*thiol\*\*\* ester. In some embodiments the catalyst is an organic base. In some embodiments, the catalyst can be 1,8-diazabicyclo[5.4.0]undec-7-ene. (What other catalysts may be used?)

DETD The reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can occur in a batch reactor or a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present

invention.

DETD The time required for the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be any reaction time required to form the described hydroxy sulfide-containing ester. Generally, the reaction time is at least 15 minutes. In some embodiments, the reaction time ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; or alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the process to produce the hydroxy sulfide-containing ester further comprises a step to remove the residual \*\*\*mercaptan\*\*\* after reacting the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester. In some embodiments the hydroxy sulfide-containing ester is vacuum stripped. In some embodiments, the hydroxy sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas to remove the \*\*\*mercaptan\*\*\*. In some embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy sulfide-containing ester comprises less than 5 weight percent of the \*\*\*mercaptan\*\*\*. In other embodiments, the stripped or sparged hydroxy sulfide-containing ester comprises less than 2 weight percent of the \*\*\*mercaptan\*\*\*; alternatively, less than 1 weight percent of the \*\*\*mercaptan\*\*\*; or alternatively, less than 0.5 weight percent of the \*\*\*mercaptan\*\*\*.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be performed at any reaction temperature capable of forming the hydroxy sulfide-containing ester. In some embodiments, the reaction temperature is greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C.

to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be performed at any reaction pressure that maintains the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester in a substantially liquid state. In some embodiments, the reaction pressure ranges from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD In another aspect, the process to produce a hydroxy sulfide-containing ester produces a hydroxy sulfide-containing ester having an \*\*\*epoxide\*\*\* group to sulfide group molar ratio less than 2.

Other hydroxy sulfide-containing ester \*\*\*epoxide\*\*\* group to sulfide group molar ratios are described herein. (The next passage needs to be incorporated into the hydroxy \*\*\*thiol\*\*\* ester section along with the first sentence of this paragraph.) Alternatively, the hydroxy sulfide-containing ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy sulfide-containing ester can be substantially free of \*\*\*epoxide\*\*\* groups.

DETD As an embodiment of the present invention, processes for producing a sulfonic acid-containing ester and for producing a sulfonate-containing ester are advantageously provided. Generally, the process for producing the sulfonic acid-containing ester comprises the steps of contacting a \*\*\*thiol\*\*\* ester and an oxidizing agent and oxidizing at least one \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester to produce a sulfonic acid group. The process for producing the sulfonate-containing ester comprises the steps of contacting a sulfonic acid-containing ester with a base and forming a sulfonate-containing ester.

DETD In an embodiment, the process to prepare a sulfonic acid-containing ester comprises the steps of contacting the \*\*\*thiol\*\*\* ester and the oxidizing agent and oxidizing the \*\*\*thiol\*\*\* ester to produce the sulfonic acid-containing ester. Generally the oxidizing agent oxidizes at least one \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\*

ester to a sulfonate group. The process to produce the sulfonic acid-containing ester composition can be applied to any \*\*\*thiol\*\*\* ester described herein to prepare any sulfonic acid-containing ester described herein. In some embodiments, the \*\*\*thiol\*\*\* ester includes a hydroxy group. For example, the \*\*\*thiol\*\*\* ester can be any hydroxy \*\*\*thiol\*\*\* ester described herein. The oxidizing agent can be any oxidizing agent described herein.

DETD In some aspects, the oxidation of the \*\*\*thiol\*\*\* ester occurs in the presence of a solvent. In some aspects, the solvent is water.

DETD The oxidizing agent that is contacted with the \*\*\*thiol\*\*\* ester can be any oxidizing agent capable of oxidizing a \*\*\*thiol\*\*\* group to a sulfonic acid group. In some embodiments, the oxidizing agent is oxygen. In other embodiments, the oxidizing agent is chlorine. In other embodiments, the oxidizing agent is dimethyl sulfoxide. In yet other embodiments, the oxidizing agent is a combination of a hydrogen halide and a catalytic amount of a dialkyl sulfide, such as dimethyl sulfoxide. Other suitable oxidizing agents will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed at any temperature capable of converting the \*\*\*thiol\*\*\* ester to a sulfonic acid-containing ester. In some embodiments, the \*\*\*thiol\*\*\* ester is oxidized a temperature greater than -20.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C.

DETD The time required for the oxidation of the \*\*\*thiol\*\*\* ester can be any time required to form the desired sulfonic acid-containing ester. Generally, the time required for the oxidation of the \*\*\*thiol\*\*\* ester is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In some embodiments, the time required for the oxidation of the \*\*\*thiol\*\*\* ester ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; alternatively, from 45 minutes to 3 hours.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed at

any pressure that maintains the \*\*\*thiol\*\*\* ester and the oxidation agent in the proper state, which is not always a liquid state, to oxidize the \*\*\*thiol\*\*\* ester to a sulfonic acid-containing ester. For example, when the oxidation agent is chlorine, the chlorine can be in the gaseous state. In some embodiments, the oxidation of the \*\*\*thiol\*\*\* ester can be performed at a pressure ranging from 0 psig to 2000 psig. In other embodiments, the oxidation of the \*\*\*thiol\*\*\* ester can be performed at a pressure ranging from 0 to 1000 psig; or alternatively, 0 to 500 psig.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed in a batch reactor or a continuous reactor, as described herein. Additionally, the process to produce the sulfonic acid-containing ester can comprise additional process steps as recognized by those skilled in the art.

DETD The formation of the sulfonate-containing ester can be performed at any temperature capable of converting the sulfonic acid group of the sulfonic acid-containing ester to a sulfonate group. In some embodiments, the sulfonate-containing ester is formed at a temperature greater than -20.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C. In yet other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature ranging from 0.degree. C. to 250.degree. C.; alternatively, from 0.degree. C. to 150.degree. C.; or alternatively, from 20.degree. C. to 100.degree. C.

DETD A preferred sulfur-containing vegetable oil is MVO available from Chevron Phillips Chemical Co. under the tradename Polymercaptan 358. Polymercaptan 358 is made by the free radical addition of hydrogen sulfide to the double bonds in soybean oil. Typically, Polymercaptan 358 has a \*\*\*thiol\*\*\* sulfur content of 5 to 10% and equivalent weights of 640 to 320, respectively.

DETD Another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a MHVO such as mercapto-hydroxy soybean oil. As described herein, a preferred mercapto-hydroxy soybean oil is made by the free radical addition of hydrogen sulfide to epoxidized

soybean oil. Typically, the mercapto and hydroxy functionalities are equal and the \*\*\*mercaptan\*\*\* content is about 8.3% \*\*\*thiol\*\*\* sulfur. The equivalent weight of this material is 192, which includes both mercapto and hydroxy functionalities.

DETD Yet another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a CMVO such as sulfur cross-linked mercaptanized soybean oil. Sulfur cross-linked mercaptanized soybean oil is made by the addition of elemental sulfur to mercaptanized soybean oil. In this process, a portion of the \*\*\*mercaptan\*\*\* groups are consumed as cross-linking sites for the sulfur. Typical sulfur cross-linked mercaptanized soybean oil products by Chevron Phillips Chemical Co. include Runs #22, 194, 195, 196 and 197 and have a \*\*\*thiol\*\*\* sulfur content ranging from about 8.0% to 1.4% and equivalent weights ranging from about 400 to about 2250, respectively.

DETD For epoxy polymer encapsulated CRF material made from sulfur-containing vegetable oil, it has been found that the use of a tertiary amine catalyst is highly preferred. The amount used is such to be sufficient to give the desired reaction rate for the production of the encapsulated slow release fertilizer product. A non-limiting example of a suitable amine catalyst is diazobicycloundecacene also known as 1,8-diazabicyclo[5,4,0]undec-7-ene [CAS# \*\*\*6674-22-2\*\*\* ] or "DBU", which is preferably used in the range of about 0.1% to 0.5% by weight of the coating. Other suitable catalyst materials will be apparent to those of ordinary skill in the art.

DETD The preferred sulfur-containing vegetable oil to be used in production of an epoxy polymer coated CRF material is MHVO such as mercapto-hydroxy soybean oil. One such material is mercapto-hydroxy soybean oil known as MHSO 566-84 produced by Chevron Phillips Chemical Co. This preferred material contains 8.33% \*\*\*thiol\*\*\* sulfur, with an equivalent weight of 384, based upon the \*\*\*mercaptan\*\*\* functionality.

DETD The unsaturated ester used as a feedstock to produce the \*\*\*thiol\*\*\* ester compositions described herein can be described using a number of different methods. One method of describing the unsaturated ester feedstock is by the number of ester groups and the number of carbon-carbon double bonds that comprise each unsaturated ester

oil molecule. Suitable unsaturated ester used as a feedstock to produce the \*\*\*thiol\*\*\* ester compositions described herein minimally comprise at least 1 ester group and at least 1 carbon-carbon double bond. However, beyond this requirement, the number of ester groups and carbon-carbon double bonds comprising the unsaturated esters are independent elements and can be varied independently of each other. Thus, the unsaturated esters can have any combination of the number of ester groups and the number of carbon-carbon double bonds described separately herein. Suitable, unsaturated esters can also contain additional functional groups such as alcohol, aldehyde, ketone, epoxy, ether, aromatic groups, and combinations thereof. As an example, the unsaturated esters can also comprise hydroxy groups. An example of an unsaturated ester that contains hydroxy groups is castor oil. Other suitable unsaturated esters will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the unsaturated \*\*\*thiol\*\*\* ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD In some embodiments, suitable polyols include 1,2-ethanediol, 1,3-propanediol, 1,4- \*\*\*butanediol\*\*\*, 1,5-pentanediol, 1,6-hexanediol, dimethylolpropane, neopentylpropane, 2-propyl-2-ethyl-1,3-propanediol, 1,2-propanediol, 1,3- \*\*\*butanediol\*\*\*, diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, tripropylene glycol, and polypropylene glycol; cyclohexanedimethanol, 1,3-dioxane-5,5-dimethanol; and 1,4-xylenedimethanol and 1-phenyl-1,2-ethanediol, trimethylolpropane, trimethylolpropane, trimethylolbutane, glycerol, 1,2,5-hexanetriol, pentaerythritol, ditrimethylolpropane, diglycerol, ditrimethylolpropane, 1,3,5-trihydroxybenzene, 1,4-xylenedimethanol, and 1-phenyl-1,2-ethanediol, or any combination thereof. In further embodiments, the polyol is glycerol, pentaerythritol, or mixtures thereof. In other embodiments, the polyol is glycerol, or alternatively pentaerythritol.

DETD Specific carboxylic acids used as a component of the carboxylic acid composition used to produce the unsaturated ester oil can have from 3 to 30 carbon atoms per carboxylic acid molecule. In some embodiments the carboxylic acid is linear. In some embodiments the carboxylic acid is branched. In some embodiments the carboxylic acid is a mixture of linear and branched carboxylic acids. In some embodiments the carboxylic acid can also comprise additional functional groups including alcohols, aldehydes, ketones, and \*\*\*epoxides\*\*\*, among others.

DETD Minimally, the epoxidized unsaturated ester comprises at least one \*\*\*epoxide\*\*\* group. In an embodiment the epoxidized unsaturated ester comprises at least 2 \*\*\*epoxide\*\*\* groups; alternatively, at least 3 \*\*\*epoxide\*\*\* groups; or alternatively, at least 4 \*\*\*epoxide\*\*\* groups.

from 2 In other embodiments, the epoxidized unsaturated ester comprises to 9 \*\*\*epoxide\*\*\* groups; alternatively, from 2 to 4 \*\*\*epoxide\*\*\* groups; alternatively, from 3 to 8 \*\*\*epoxide\*\*\* groups; or alternatively, from 4 to 8 \*\*\*epoxide\*\*\* groups.

DETD In some embodiments, the unsaturated ester comprises a mixture of epoxidized unsaturated esters. In this aspect, the number of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester is best described as an average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the epoxidized unsaturated esters have an average of at least 1.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; or alternatively, an average of at least 3 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In other embodiments, the epoxidized unsaturated esters have average of from 1.5 to 9 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of from 3 to 8 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of from 2 to 4 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; or alternatively, from 4 to 8 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule.



DETD The \*\*\*thiol\*\*\* composition can include an average of greater than 0 to about 4 \*\*\*epoxide\*\*\* groups per triglyceride. The \*\*\*thiol\*\*\* composition can also include an average of greater than 1.5 to about 9 \*\*\*epoxide\*\*\* groups per triglyceride.

DETD \*\*\*Mercaptans\*\*\*

DETD Within some embodiments, an unsaturated ester or an epoxidized unsaturated ester is contacted with \*\*\*mercaptan\*\*\*. Within these embodiments, the \*\*\*mercaptan\*\*\* can be any \*\*\*mercaptan\*\*\* comprising from 1 to 20 carbon atoms. Generally, the \*\*\*mercaptan\*\*\* can have the following structure: HS--R<sub>3</sub> wherein R<sub>3</sub> is a C1 to C20 organyl groups or a C1 to C20 hydrocarbyl groups. In further embodiments the R<sub>3</sub> can be a C2 to C10 organyl group or a C2 to C10 hydrocarbyl group. In some embodiments, the \*\*\*mercaptan\*\*\* composition comprises a solvent. In one aspect, the \*\*\*mercaptan\*\*\* composition comprises at least one other functional group.

DETD The at least one other functional group can be selected from several different groups. For example, the at least one other functional group is an alcohol group, a carboxylic alcohol group, a carboxylic ester group, an amine group, a sulfide group, a \*\*\*thiol\*\*\* group, a methyl or ethyl ester of a carboxylic acid group, or combinations thereof. Other types of functional groups will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In some embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of 3-mercaptopropyl-trimethoxysilane, 2-mercaptopyridine, 4-mercaptopyridine, 2-mercaptopyrimidine, mercaptopyruvic acid, mercaptosuccinic acid, 2-mercaptonicotinic acid, 6-mercaptonicotinic acid, 2-mercaptophenol, 4-mercaptophenol, 3-mercapto-1,2-propanediol, 3-mercapto-1,2-propanediol, 3-mercapto-1-propanesulfonic acid, 1-mercapto-2-propanol, 3-mercapto-1-propanol, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzyl alcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethanesulfonic acid, 2-mercaptoethanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 16-mercaptohexadecanoic acid, 6-mercapto-1-hexanol, 4'-mercaptoacetanilide, mercaptoacetic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptothiazoline, 3-mercapto-1H-1,2,4-triazole, 11-mercaptoundecanoic acid, 11-mercapto-1-undecanol, or combinations thereof.

DETD In some embodiments, the \*\*\*mercaptan\*\*\* is selected from

the group  
consisting of beta-mercaptoethanol, 2-mercaptophenol, 3-  
mercaptophenol,  
4-mercaptophenol, 1-mercapto-2-propanol, 1-mercapto-3-propanol,  
mercaptoacetic acid, 2-mercaptopropionic acid, 3-  
mercaptopropionic acid,  
2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic  
acid,  
2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-  
butanol,  
2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 6-mercapto-  
hexanol,  
3-mercapto-1,2-propanediol, mercaptosuccinic acid, and mixtures  
thereof.  
In further embodiments, the \*\*\*mercaptan\*\*\* is selected from  
the  
group consisting of beta-mercaptoethanol, 1-mercapto-2-propanol,  
1-mercapto-3-propanol, 2-mercaptobenzylalcohol, 3-mercapto-2-  
butanol,  
4-mercapto-1-butanol, 6-mercapto-hexanol, 3-mercapto-1,2-  
propanediol,  
and mixtures thereof. In further embodiments, the  
\*\*\*mercaptan\*\*\* is  
selected from the group consisting 2-mercaptophenol, 3-  
mercaptophenol,  
4-mercaptophenol, and mixtures thereof. In yet further  
embodiments, the  
\*\*\*mercaptan\*\*\* is selected from the group consisting  
mercaptoacetic  
acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid,  
2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic  
acid,  
mercaptosuccinic acid, and mixtures thereof.  
DETD Within some embodiments, the inventive compositions described  
herein  
are reacted with an isocyanate compound to produce a  
polythiourethane  
composition. The isocyanate may be any isocyanates capable of  
reacting  
with the \*\*\*thiol\*\*\* esters, hydroxy \*\*\*thiol\*\*\* esters,  
and a  
cross-linked \*\*\*thiol\*\*\* esters described herein to form a  
polyurethane composition. Generally, the isocyanate compound has  
at  
least two isocyanate groups.  
DETD In order to quantitatively measure the \*\*\*thiol\*\*\* sulfur,  
the  
\*\*\*thiol\*\*\* sulfur analyses were conducted using silver  
nitrate  
titration in accordance with ASTM D3227, with the following  
modifications designed to minimize probe fouling by silver salts:  
the  
samples were diluted in a known mass of tetrahydrofuran. The  
silver  
nitrate concentration was 0.01 N standardized against potassium  
iodide.  
DETD \*\*\*Thiol\*\*\* sulfur was analyzed by three different tests.  
The first  
test used was the modified ASTM D3227, which resulted in a  
\*\*\*thiol\*\*\*

sulfur measurement of 4.64%. The second test used to measure the  
 \*\*\*thiol\*\*\* sulfur was SLP-1204, which is a test developed by  
 Chevron Phillips Chemical Company LLP. By using the SLP-1204 test, the  
 resulting \*\*\*thiol\*\*\* sulfur measurement was 4.28%. Lastly, the total  
 sulfur was measured by combustion analysis, which resulted in a total sulfur  
 measurement of 4.27%.  
 DETD Vegetable oil (42 kg) was charged to a 100-gallon holding  
 vessel. The vessel was purged with nitrogen and returned to atmospheric  
 pressure. Hydrogen sulfide (174 kg) was charged to the holding vessel. The  
 vessel temperature was controlled from 25-30.degree. C. while the  
 pressure was typically maintained between 380-400 psig. The reactants were  
 continuously rolled from the holding tank through a stainless  
 steel tubular photochemical reactor containing a 7.5 KW Hanovia medium  
 pressure mercury lamp contained within a quartz tube. Reactor  
 temperature, pressure, and composition were monitored over the  
 course of the reaction. The reaction time was dependent upon reaching a  
 desired composition of \*\*\*thiol\*\*\* sulfur. Upon completion, the  
 unreacted hydrogen sulfide was slowly vented from the system. Residual  
 H.sub.2S was removed at 100.degree. C. and reduced pressure while passing  
 nitrogen through a nitrogen sparge tube. The product was drained  
 from the bottom of the reactor into a clean drum. The \*\*\*thiol\*\*\*  
 sulfur measurements were 11.0% when using the modified ASTM D3227, 8.74%  
 when using SLP-1204, and the total sulfur was 11.21% when using  
 combustion analysis (total sulfur).  
 DETD The resulting mercaptanized soybean oil was subjected to  
 nitrogen sparging under reduced pressure at 100.degree. C. for a period of  
 4 hours to remove any residual hydrogen sulfide. The \*\*\*thiol\*\*\*  
 D3227, sulfur measurements were 13.0% when using the modified ASTM  
 9.82% when using SLP-1204, and 11.69% when using combustion analysis.  
 DETD Table 1 provides the properties of the mercaptanized soybean oil  
 produced in examples 1-3.

TABLE 1

Mercaptanized Soybean Oil Product Properties

C.dbd.C	Cyclic Sulfide to ***Thiol***		
	***Thiol*** Sulfur.sup..dagger. Group		
Example	to ***Thiol*** (wt %)	groups Molar Ratio	Molar Ratio

1	4.28	0.02	2.79
2	11.0	0.03	0.26
3	13.0	0.03	0.51

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by the modified ASTM

D3227

DETD Soybean oil was charged to a 1000 gallon stirred reactor.

Hydrogen

sulfide was then charged to the reactor. After the hydrogen sulfide was charged to the reactor, the stirrers and the UV lamps were turned on and

the reaction allowed to build temperature and pressure as the reaction

proceed. The reaction was continued until a minimum \*\*\*thiol\*\*\* sulfur content of 8 weight percent was achieved. After reaction

was completion, the excess hydrogen sulfide was flashed from the reactor.

For runs 2-5, the mercaptanized soybean oil product underwent an additional hydrogen sulfide stripping step comprising stripping hydrogen

sulfide from the product under vacuum, 50 mm Hg, at 250.degree.

F. (only

true for runs 2-5).

DETD Table 3 provides the details of the analysis of the

mercaptanized

soybean oil producing in the five 1000 gallon reactor runs.

TABLE 3

1000 gallon reactor Mercaptanized Soybean Oil Product Properties

	***Thiol***	Cyclic Sulfide to	***Thiol***	Side Chain C.dbd.C
to				

Run	***Thiol***	Containing	Sulfur.sup..dagger. Group
Number	(wt %)	Molar Ratio	Groups
1	9.3	--	
2	9.6	0.04	
3	9.2	0.03	
4	9.3	0.03	
5	10.1	0.03	

	groups	Molar Ratio	(%)

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by Raman spectroscopy

Mercaptanized Castor Bean Oil

DETD The analytical properties of the two mercaptanized castor oil products

are provide in Table 4.

TABLE 4

Mercaptanized Castor Oil Product Properties

Containing	***Thiol***	C.dbd.C to	Side Chain

\*\*\*Thiol\*\*\*

Groups

Example	(wt %)	Molar Ratio	(%)
1	6.4	0.52	64.1
2	7.4	0.26	77.7

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by Raman spectroscopy

Mercaptohydroxy Soybean Oil Synthetic Procedure

DETD Epoxidized Soybean Oil (700 g, .about.0.7 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.7 g, 30.5 mmol) were charged

to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630

psig. Hydrogen sulfide (H.sub.2S, 132.0 g, 3.87 mol) was then pressured

into the stirred reactor contents through a dip tube in the liquid

space. The reaction mixture was heated and maintained at 85.degree. C.

with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 351 psig to 219 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S

was slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under

vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 7.53

wt. %, 2.5 SH/molecule, or 2.35 meq SH/g. Combustion analysis indicated

C, 64.37%; H, 10.20%; N, <0.15%; and S, 9.51%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure

tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in

the liquid space. The reaction mixture was heated and maintained at

97.degree. C. with stirring for 14 hrs, during which time the reactor

pressure decreased from a maximum of 509 psig to 229 psig. The stirrer

was stopped and while still warm (90-95.degree. C.), excess H.sub.2S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under

under

vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual  
H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content  
of 4.14 wt. %, 1.4 SH/molecule, or 1.29 meq SH/g. Combustion analysis  
indicated C, 65.18%; H, 10.17%; N, <0.15%; and S, 7.80%.  
DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and  
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
charged to a 1-L Hastelloy C autoclave reactor, and the vessel was  
pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99  
mol) was then pressured into the stirred reactor contents through a dip  
tube in the liquid space. The reaction mixture was heated and maintained  
at 85.degree. C. with stirring for 10 hrs, during which time the  
reactor pressure decreased from a maximum of 578 psig to 489 psig. The  
stirrer was stopped and while still warm (80-85.degree. C.), excess  
H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space  
was then swept with N.sub.2 for 1 hr and the reactor contents drained warm  
(80-85.degree. C.). The reaction product was N.sub.2 sparged  
under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
residual H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*\*thiol\*\*\* sulfur (titration with modified ASTM D3227)  
content of 8.28 wt. %, 2.8 SH/molecule, or 2.58 meq SH/g. Combustion  
analysis indicated C, 65.24%; H, 9.52%; N, 0.18%; and S, 9.53%.  
DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and  
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
charged to a 1-L Hastelloy C autoclave reactor that was pressure tested  
to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then  
pressured into the stirred reactor contents through a dip tube in the  
liquid space. The reaction mixture was heated and maintained at  
85.degree. C. with stirring for 12 hrs, during which time the reactor pressure  
decreased from a maximum of 587 psig to 498 psig. The stirrer was  
stopped and while still warm (80-85.degree. C.), excess H.sub.2S  
was slowly vented to a low-pressure flare. The reactor vapor space  
was then swept with N.sub.2 for 1 hr and the reactor contents drained warm  
(80-85.degree. C.). The reaction product was N.sub.2 sparged  
under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content  
of 8.24 wt. %, 2.8 SH/molecule, or 2.57 meq SH/g. Combustion analysis  
indicated C, 63.39%; H, 10.01%; N, <0.15%; and S, 8.76%.  
DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and  
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
charged to a 1-L Hastelloy C autoclave reactor, and the vessel was  
pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99  
mol) was then pressured into the stirred reactor contents through a dip  
tube in the liquid space. The reaction mixture was heated and maintained  
at 85.degree. C. with stirring for 8 hrs, during which time the  
reactor pressure decreased from a maximum of 606 psig to 537 psig. The  
stirrer was stopped and while still warm (80-85.degree. C.), excess  
H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space  
was then swept with N.sub.2 for 1 hr and the reactor contents drained warm  
(80-85.degree. C.). The reaction product was N.sub.2 sparged  
under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
residual H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content  
of 7.34 wt. %, 2.5 SH/molecule, or 2.29 meq SH/g. Combustion analysis  
indicated C, 64.47%; H, 10.18%; N, <0.15%; and S, 8.40%.  
DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and  
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
charged to a 1-L Hastelloy C autoclave reactor that was pressure tested  
to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then  
pressured into the stirred reactor contents through a dip tube in the  
liquid space. The reaction mixture was heated and maintained at  
85.degree. C. with stirring for 6 hrs, during which time the reactor pressure  
decreased from a maximum of 586 psig to 556 psig. The stirrer was  
stopped and while still warm (80-85.degree. C.), excess H.sub.2S  
was slowly vented to a low-pressure flare. The reactor vapor space  
was then swept with N.sub.2 for 1 hr and the reactor contents drained warm  
(80-85.degree. C.). The reaction product was N.sub.2 sparged  
under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
residual H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content

of 5.93 wt. %, 2.0 SH/molecule, or 1.85 meq SH/g. Combustion analysis indicated C, 65.26%; H, 10.19%; N, <0.15%; and S, 8.43%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 595 psig to 554 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 5.36 wt. %, 1.8 SH/molecule, or 1.67 meq SH/g. Combustion analysis indicated C, 65.67%; H, 10.17%; N, 0.34%; and S, 9.84%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 519 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration with AgNO.sub.3) content of 5.85 wt. %, 2.0 SH/molecule, or 1.82 meq SH/g. Combustion analysis indicated



C, 65.09%; H, 10.15%; N, 0.35%; and S, 10.63%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 2 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 508 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 5.07 wt. %, 1.7 SH/molecule, or 1.58 meq SH/g. Combustion analysis indicated C, 63.96%; H, 10.01%; N, 0.35%; and S, 11.22%.

DETD Table 5 provides the properties of the mercaptohydroxy soybean oil samples produced in Examples 1-10.

TABLE 5

per Example	***Epoxides***		***Mercaptan***		
	Reaction	Reaction	Sulfur	SH per	groups left
	***Epoxide*** Time (hrs) molecule.sup.3	:SH Molar Ratio	Temp (.degree. C.) (wt. %).sup.1	molecule.sup.2	
1	0	N/A	N/A	0	4.3
--					
2	8	85	7.53	2.5	1.8
3	0.72 14	97	4.14	1.4	2.9
4	2.07 10	85	8.28	2.8	1.5
5	0.54 12	85	8.24	2.8	1.5
6	0.54 8	85	7.34	2.5	1.8
7	0.72 6	85	5.93	2.0	2.3

8	1.15	4	85	5.36	1.8	2.5
	1.40					
9	1.15	4	85	5.85	2.0	2.3
	1.529					
10	2		85	5.07	1.7	2.6

.sup.1Thiol sulfur was determined by silver nitrate oxidation using ASTM D 3227

.sup.2Determined by Wt. % \*\*\*thiol\*\*\* sulfur

.sup.3Determined by subtracting the SH/molecule from the starting material

\*\*\*epoxide\*\*\* content

DETD Epoxidized soybean oil and the catalyst were charged to a 1-L Hastelloy

C autoclave reactor, and the vessel was pressure tested to 1000 psig.

Hydrogen sulfide was then pressured into the stirred reactor contents

through a dip tube in the liquid space. The reaction mixture was heated

and maintained at temperature a set period of time with stirring for 12

hrs. During the reaction time the reactor pressure usually decreased. At

the end of the reaction time, the stirrer was stopped and excess H.sub.2S was slowly vented while the reaction mixture was warm to

a low-pressure flare. The reactor vapor space was then swept with N.sub.2

for 1 hr and the reactor contents drained. The reaction product was

N.sub.2 sparged under vacuum (<50 mmHg) at 100.degree. C. for 16 hrs to

remove residual H.sub.2S. Table 6 provides the reaction conditions used

to produce the mercaptohydroxy soybean oils for several runs and the

\*\*\*thiol\*\*\* sulfur content of the mercaptohydroxy soybean oils

produced.

TABLE 6

#### Mercaptohydroxy Soybean Oil Production Runs

Run	Epoxidized Soybean Oil Temperature (g)	Catalyst Time (g)	H.sub.2S (g)	H.sub.2S: Sulfur.sup.a Molar Ratio	***Epoxide*** Sulfur.sup.a (.degree. C.)	
(minutes)	(wt. %)					
556-41.sup..dagger.	249.6		1.950	214.0	5.86	64
728	5.69					
556-53.sup..dagger.	250.0		2.000	213.0	5.81	100
370	9.04					
556-47.sup..dagger.	250.5		1.050	213.0	5.81	101
720	10.47					
407-81D.sup..dagger.	500.0		4.200	255.0	3.49	85

480	7.53					
407-86.sup..dagger.	600.0	5.000	204.0	2.07	85	
600	8.28					
556-79.sup..dagger-dbl.	250.0	2.600	214.0	5.83	100	
720	6.68					
556-80.sup..dagger-dbl.	251.0	5.000	214.0	5.81	100	
720	9.51					

.sup..dagger.Catalyst was DBU  
 .sup..dagger-dbl.catalyst was triethylamine (TEA)  
 .sup.aThiol sulfur measured by silver nitrate titration using modified ASTM D

3227  
 DETD Run number 407-86 was subjected to the sodium methoxide methanolysis procedure and subsequently analyzed by GC/MS. The GS/MS analysis indicated that the product had \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio of approximately 0.14. The methanolysis data also indicated that an average of 80.4 percent of the product mercaptohydroxy soybean oil contained sulfur.  
 DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (9.6 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 99.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (904.8 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 6.33 wt. % (by modified ASTM D3227). The elemental combustion analysis was 70.19%; C, 10.37%; H, and 11.21%; S.  
 DETD Mercaptanized soybean oil (900.0 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (36.0 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 36 hrs. H.sub.2S evolution was observed. The reaction product (825.6 g) was sparged with N.sub.2 under vacuum at 90.degree. C. for 36 hrs to remove residual H.sub.2S. The reaction product was then sparged with N.sub.2 under vacuum at 110.degree. C. for 3 hrs to remove residual

H.sub.2S.

The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 2.36 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.90%; C, 11.07%; H, and 12.25%; S.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (18.0 g). The reaction mixture was heated to 125.degree. C.

C. until sulfur dissolved and then cooled to 101.degree. C.

Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (901.5 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 4.9 wt. % (by modified ASTM D3227). The elemental combustion analysis was 69.58%; C, 11.25%; H, and 11.31%; S.

DETD Mercaptanized soybean oil (900.2 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (45.0 g). The reaction mixture was heated to 125.degree. C.

C. until sulfur dissolved and then cooled to 100.degree. C.

Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (915.0 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 1.41 wt. % (by modified ASTM D3227).

The elemental combustion analysis was 68.35%; C, 10.98%; H, and 13.28%; S.

DETD Numerous polythiourethane compositions were prepared by reacting a \*\*\*thiol\*\*\* ester composition with a diisocyanate in the presence of a catalyst by using the processes described herein for preparing such polythiourethane compositions. The compositions were produced using the different variables of feedstocks, diisocyanates, stoichiometry, and catalysts shown in Table 8. Once every combination of variable was used, over 1200 compositions were produced. Each of the feedstocks were reacted with each of the diisocyanates at each of the stoichiometries with each of the catalysts listed to produce the 1200+

compositions. The stoichiometry was based upon a \*\*\*thiol\*\*\* ester composition (MSO, MHSO, CMSO, MCO) active hydrogen ( \*\*\*thiol\*\*\* and hydroxyl group) to diisocyanate equivalent ratio. For example, castor oil was reacted with toluene diisocyanate at a stoichiometric value of 1.25 while using Jeffol.RTM. A-480 as the catalyst. As another example, a \*\*\*thiol\*\*\* ester composition was reacted with methane diisocyanate at a stoichiometric value of 0.9 while using the DABCO catalyst.

DETD In the first MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate at a \*\*\*thiol\*\*\* to isocyanate mole ratio of 0.95. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the second MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate M20S at a \*\*\*thiol\*\*\* to isocyanate mole ratio of 1.00. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the polythiourethane compositions, the feedstock \*\*\*thiol\*\*\* ester compositions that were used included MSO (mercaptanized soybean oil), MHSO (mercaptohydroxy soybean oil), CMSO (cross-linked mercaptanized soybean oil), castor oil, and MCO (mercaptanized castor oil). The diisocyanates that were used to produce these compositions included MDI (4,4'-methylenebis(phenyl) diisocyanate), HMDI (4,4'-methylenebis(cyclohexyl) diisocyanate, which is also known as

hydrogenated MDI), TDI (tolylene 2,4-diisocyanate), HDI (1,6-diisocyanatohexane, which is also known as hexamethylene diisocyanate), and Luprinate.TM. M20S (which is an oligomerized form of MDI and is also referred to as polymeric MDI that is produced by BASF Corporation). The catalysts that were used included DABCO (diazabicyclooctane--di-tertiary amine), DBTDL (dibutyl tin dilaurate--organometallic catalyst), Jeffol.RTM.t A-480 (which is a tertiary amine polyol produced by Huntsman Based Chemicals), and BDMA (benzyltrimethylamine). DETD In the Fertilizer Examples, the following materials were used:

A: Fertilizer particles--granular fertilizer grade urea, SGN 250, commercially available from Agrium;  
B1: Mercaptanized soybean oil (an example of MVO discussed above)--Polymercaptan 358, available from Chevron Phillips Chemical Co.; 8.65% \*\*\*thiol\*\*\* sulfur; 370 equivalent weight; viscosity of 510.6 cSt @ 21.degree. C.;  
B2: Mercapto-hydroxy soybean oil (an examples of MHVO discussed above)--A mercapto-hydroxy soybean oil made by the free radical addition of hydrogen sulfide to epoxidized soybean oil; the mercapto and hydroxy functionalities are equal; 8.335% \*\*\*thiol\*\*\* sulfur; equivalent weight 192 (including both mercapto and hydroxy functionalities);  
B3: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; \*\*\*thiol\*\*\* sulfur content 6.33%; equivalent weight 506;  
B4: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; \*\*\*thiol\*\*\* sulfur content 7.64%; equivalent weight 419; cross-linkcross-link  
C1: Isocyanate #17--A polymeric MDI, commercially available from BASF Canada, equivalent weight of 133;  
C2: Epoxy resin--5 minute epoxy resin, commercially available from ITW Devcon, Danvers, Mass. 01923 USA, equivalent weight 198;  
D1: Organic additive--Gulftene C30-HA alpha olefin wax, commercially available from Chevron Phillips Chemical Co., melting point 65.degree. C.--80.degree. C.;  
D2: Organic additive--Calwax 170, a microcrystalline wax commercially available from Calwax Corporation;  
E: Cross-linking agent--Jeffol A480, commercially available from Huntsman Polyurethanes; equivalent weight of 120; functionality 4.0; viscosity of 4000 cPs @25 C;

F1: Amine catalyst: Exp-9, commercially available from Huntsman Polyurethanes;  
 and  
 F2: Amine catalyst: 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), CAS# \*\*\*6674-22-2\*\*\*

DETD Analysis of the \*\*\*Thiol\*\*\* Containing Esters, Hydroxy  
 \*\*\*Thiol\*\*\* Containing Esters and Cross-Linked \*\*\*Thiol\*\*\*  
 Containing Ester

DETD Particular aspects of the \*\*\*thiol\*\*\* containing esters,  
 hydroxy \*\*\*thiol\*\*\* containing esters, cross-linked \*\*\*thiol\*\*\*  
 ester,  
 unsaturated esters and epoxidized unsaturated esters are measured  
 particular analytical techniques. \*\*\*Thiol\*\*\* sulfur values  
 were  
 obtained using a silver nitrate titration as described in ASTM  
 D3227 or  
 by Raman spectroscopy. Carbon-carbon double bond to \*\*\*thiol\*\*\*  
 group molar ratio, cyclic sulfide to \*\*\*thiol\*\*\* group molar  
 ratios  
 were determined by .sup.13C NMR and/or GC analysis of the  
 \*\*\*thiol\*\*\*  
 containing ester or hydroxy \*\*\*thiol\*\*\* containing ester side  
 chains.

DETD \*\*\*Thiol\*\*\* Sulfur Content by Raman Spectroscopy  
 DETD \*\*\*Thiol\*\*\* sulfur content was measured by both silver  
 nitrate  
 titration, ASTM D3227, and/or Raman spectroscopy. The Raman  
 spectroscopy  
 method is practiced by measuring the Raman spectra of the  
 \*\*\*thiol\*\*\*  
 containing ester, hydroxy \*\*\*thiol\*\*\* containing ester,  
 cross-linked  
 \*\*\*thiol\*\*\* ester and comparing the spectra to calibration  
 standards  
 containing know \*\*\*thiol\*\*\* compounds having know amounts of  
 \*\*\*thiol\*\*\* groups. Generally, the calibration standard  
 \*\*\*thiol\*\*\*  
 compound has a similar structure to the \*\*\*thiol\*\*\*  
 containing  
 esters analyzed.

DETD The \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\*  
 containing esters and cross-linked \*\*\*thiol\*\*\* ester  
 \*\*\*thiol\*\*\*  
 content were determined by comparing the Raman spectra of the  
 \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\*  
 containing  
 esters and cross-linked \*\*\*thiol\*\*\* ester to calibration  
 standards  
 prepared from mercaptanized methyl oleate diluted in soybean oil  
 to  
 known \*\*\*thiol\*\*\* sulfur contents. \*\*\*Thiol\*\*\* sulfur  
 calibration standards were prepared using standards using various  
 known  
 concentration of mercaptanized methyl oleate diluted in soybean  
 oil.  
 DETD Raman spectra of the calibration standards and the \*\*\*thiol\*\*\*  
 containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and  
 cross-linked \*\*\*thiol\*\*\* ester were measured using a Kaiser  
 Hololab

5000 Process Raman spectrometer, using a 785 nm laser.

\*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester samples and the \*\*\*thiol\*\*\* sulfur calibration standard Raman spectra were obtained by collecting four 10 second scans which were then processed using Holoreact software.

\*\*\*thiol\*\*\* sulfur values for the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester were then calculated using the ratio of the peak area values of the \*\*\*thiol\*\*\* SH peak (center: 2575 cm<sup>-1</sup>; area 2500-2650 cm<sup>-1</sup>), and the C.dbd.O peak (center--1745 cm<sup>-1</sup>; area--1700-1800 cm<sup>-1</sup>) and comparing them to the peak area values for the calibration standards and interpolating the containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester \*\*\*thiol\*\*\* sulfur contents. Repeatability of the \*\*\*thiol\*\*\* sulfur values as measured by Raman spectroscopy have been shown to have a standard deviation of 0.05-0.1 and a % RSD of 0.6-1.5 using 5 samples having a % \*\*\*thiol\*\*\* sulfur content ranging from 3.1-10.6 weight percent as measured over a two month period.

DETD The Raman spectroscopy technique for determining the \*\*\*thiol\*\*\* sulfur content of a \*\*\*thiol\*\*\* containing ester, hydroxy \*\*\*thiol\*\*\* containing ester, and a cross-linked \*\*\*thiol\*\*\* containing ester has been illustrated using a \*\*\*thiol\*\*\* ester produced from soybean oil. However, one skilled in the art may adapt and apply the Raman spectroscopy technique for determining the \*\*\*thiol\*\*\* sulfur content of other \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters, and a cross-linked \*\*\*thiol\*\*\* containing esters described herein.

DETD C.dbd.C to \*\*\*Thiol\*\*\* Group and Cyclic Sulfide Group to \*\*\*Thiol\*\*\* Group Molar Ratios by .sup.13C NMR

DETD Carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio and cyclic sulfide group to \*\*\*thiol\*\*\* group molar ratios were determined by .sup.13C NMR. \*\*\*Thiol\*\*\* containing ester .sup.13C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (75.5 MHz .sup.13C NMR). Peak areas were determined for the cyclic sulfide carbon



atoms,       \*\*\*thiol\*\*\*    group HS--C carbon atoms and carbon-carbon double  
bonds       carbon atoms using the .sup.13C NMR regions indicated in the  
table       below:

Functional Group	.sup.13C NMR Region	Number of Carbon Atoms/Group
Cyclic Sulfide Carbon Atoms	49-49.5 ppm	2
HS--C Carbon Atoms	40-41.5 ppm	1
C.dbd.C Carbon Atoms	120-140 ppm	2

DETD   The   \*\*\*thiol\*\*\*    containing ester cyclic sulfide to  
\*\*\*thiol\*\*\*  
group molar ratio were calculated by dividing the cyclic sulfide  
carbon   atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon  
atoms per   cyclic sulfide group) and dividing the resultant number by the  
\*\*\*thiol\*\*\*   group HS--C carbon atoms .sup.13C NMR peak area.

The       \*\*\*thiol\*\*\*    containing ester carbon-carbon double bond to  
\*\*\*thiol\*\*\*    group molar ratio were calculated by dividing the  
C.dbd.C   carbon atoms .sup.13C NMR peak area by 2 (to account for the 2  
carbon   atoms per carbon-carbon double bond) and dividing the result  
number by   the   \*\*\*thiol\*\*\*   group HS--C carbon atoms .sup.13C NMR peak  
area       Offset sample .sup.13C NMR's for soybean oil and a   \*\*\*thiol\*\*\*  
containing ester produced from soybean oil using the disclosed  
process   is provided as FIG. 1.

DETD   The NMR technique for analyzing the unsaturated ester and the  
\*\*\*thiol\*\*\*   containing ester produced from an unsaturated  
ester have   been illustrated using .sup.13C NMR on soybean oil the  
\*\*\*thiol\*\*\*  
containing ester produced from soybean oil. However, one skilled  
in the   art may adapt and apply either the .sup.13C NMR or .sup.1H NMR  
technique   to analyze the unsaturated esters and   \*\*\*thiol\*\*\*   containing  
ester       produced from the unsaturated ester described herein.

DETD   \*\*\*Epoxide\*\*\*   Group to   \*\*\*Thiol\*\*\*   Group Molar Ratios by  
.sup.13C or .sup.1H NMR

DETD   The   \*\*\*epoxide\*\*\*   group to   \*\*\*thiol\*\*\*   group molar  
ratios were  
determined using .sup.1H or .sup.13C NMR. Hydroxy   \*\*\*thiol\*\*\*  
containing ester .sup.1H or .sup.13C NMR spectra were obtained on  
a  
Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or  
equivalent spectrometer (300 MHz .sup.1H NMR-75.5 MHz .sup.13C  
NMR).  
Peak areas were determined for the   \*\*\*epoxide\*\*\*   group and  
sulfide

group using the .sup.13C and or .sup.1H regions indicated in the table below:

Functional Group	.sup.1H NMR Region	.sup.13C NMR Region	Number of Carbon Atoms/Group	Number of Hydrogen Atoms/Group
***Epoxide***	Group	2.75-3.2 ppm	53.6-56.6 ppm	2
2 Carbon Atoms				
HS--C Carbon Atoms	3.2-4 ppm	40-41.5 ppm	1	1
DETD The hydroxy group to	***thiol***	containing ester	***epoxide***	
	***thiol***	group molar ratio were calculated by dividing the	***epoxide***	
(to	***epoxide***	group carbon atoms .sup.1H NMR peak area by 2		
group	account for the 2 hydrogen atoms attached to the	***epoxide***		
	carbon atoms) and dividing the result number by the	***thiol***		
the	group HS--C carbon atom hydrogens IC NMR peak area. Similarly,			
to	hydroxy ***thiol***	containing ester	***epoxide***	group
peak	***thiol***	group molar ratio were calculated using 13H NMR		
	areas.			
DETD	The average number of	***epoxide***	group per epoxidized	
methods	unsaturated ester molecule can be determined utilizing similar			
group	utilizing either the carbonyl group carbon atom or the C--O ester			
	carbon atoms .sup.13C NMR peak areas in conjunction with the			
NMR's	***epoxide***	group .sup.13C NMR peak area. Sample .sup.1H		
	epoxidized soybean oil and a	***thiol***	containing ester	
produced	from epoxidized soybean oil 1 are provided in FIG. 2.			
DETD	The NMR technique for analyzing the epoxidized unsaturated ester			
and				
	the ***thiol***	containing ester produced from an epoxidized		
has been	unsaturated ester (a hydroxy ***thiol***	containing ester)		
	illustrated using .sup.1H NMR on epoxidized soybean oil the			
oil.	***thiol***	containing ester produced from epoxidized soybean		
	However, one skilled in the art may adapt and apply either the			
.sup.1H				
	NMR or .sup.13C NMR technique to analyze the epoxidized			
unsaturated	esters and	***thiol***	containing ester produced from the	
epoxidized				
	unsaturated ester described herein.			
DETD	Analysis of Unsaturated Esters, Epoxidized Unsaturated Esters,			
	***Thiol***	Containing Esters, and Hydroxy	***Thiol***	
Containing				
	Esters by Methanolysis			

DETD Many properties of the unsaturated esters, epoxidized  
 unsaturated  
 esters, \*\*\*thiol\*\*\* containing esters, and hydroxy  
 \*\*\*thiol\*\*\*  
 containing ester were and/or can be determined by converting the  
 complex  
 ester molecules into their component polyols and carboxylic acid  
 methyl  
 esters. The converted esters are then analyzed by gas  
 chromatography  
 (GC) and/or gas chromatography/mass spectrometry (GCMS) to  
 determine the  
 composition of the complex ester side chains. Properties that are  
 or can  
 be determined by the methanolysis followed by GC or GC/MS of the  
 that  
 carboxylic acid methyl esters include the number of side chain  
 group  
 contain \*\*\*thiol\*\*\* groups, the percent of \*\*\*thiol\*\*\*  
 group  
 sulfur, the number of (or average number) of double bonds per  
 ester  
 molecule, the molecular weight distribution (or average molecular  
 weight) of the ester side chains, the number of (or average  
 number of)  
 \*\*\*epoxide\*\*\* groups per ester molecule, the cyclic sulfide  
 to  
 \*\*\*thiol\*\*\* group molar ratio, the carbon-carbon double bond  
 to  
 \*\*\*thiol\*\*\* group molar ratio, and the \*\*\*epoxide\*\*\*  
 group to  
 \*\*\*thiol\*\*\* group molar ratio, among others.  
 DETD Depending upon the material being subjected to the methanolysis  
 procedure, there are two methanolysis procedures that were  
 practiced  
 upon the unsaturated ester, epoxidized esters, \*\*\*thiol\*\*\*  
 containing ester, and hydroxy \*\*\*thiol\*\*\* containing esters  
 described within the experimental section.  
 DETD Unsaturated esters and \*\*\*thiol\*\*\* containing ester produced  
 from  
 unsaturated ester were subjected to a hydrogen chloride based  
 methanolysis procedure. In the hydrogen chloride methanolysis  
 procedure,  
 a 50 to 100 mg sample of the \*\*\*thiol\*\*\* containing ester is  
 contacted with 3 mL of 3 N methanolic HCl and reacted for 2 hours  
 a  
 50.degree. C. The solution is then allowed to cool and the  
 neutralized  
 with a dilute sodium bicarbonate solution. The solution's organic  
 components are then extracted with ethyl ether and analyzed by GC  
 and/or  
 GC/MS. Additional details for the methanolic hydrogen chloride  
 methanolysis procedure may be found in the product specification  
 sheet  
 for methanolic HCl, 0.5 N and 3 N as supplied by Supelco.  
 DETD Epoxidized unsaturated esters and hydroxy \*\*\*thiol\*\*\*  
 containing  
 esters produced from epoxidized unsaturated esters were subjected  
 to a  
 sodium methoxide based methanolysis procedure. The sodium  
 methoxide

methanolysis procedure was based upon the procedure disclosed in U.S. Pat. No. 3,991,089. In the sodium methoxide methanolysis procedure, approximately 1 g of the ester was placed in a 50 mL vial with 5.0 mL 25% sodium methoxide in methanol, and 10 mL methanol. The mixture was shaken for approximately 1 hour at room temperature, during which time the solution became one phase. The mixture was then poured into 25 mL of distilled water. Diethyl ether, 25 mL, was added to the solution and the mixture was acidified with 0.5 N HCL to a pH of approximately 5. The organic layer was separated from the aqueous layer using a separatory funnel. The organic layer was washed successively with distilled water (15 mL) and brine solution (15 mL) and then dried over magnesium sulfate. The magnesium sulfate was separated from the organic solution by filtration and the solvent removed by rotary evaporation. DETD FIG. 3 provides a GC/MS trace of a mercaptanized soybean oil subjected to the methanolysis procedure and analyzed by GC/MS using a HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column. Table 11 provides the GC/MS trace peak assignments. TABLE 11

GC/MS Data for Methanolysis of A \*\*\*Thiol\*\*\* Containing  
Ester Produced from Soybean Oil  
GC Retention time Methyl Ester Carboxylic Acid Assignment

21.58	Methyl hexadecanoate
23.66	Methyl (C18 monoene)oate
23.74	Methyl (C18 monoene)oate
23.96	Methyl octadecanoate
26.46	Methyl (C18 Monoene monomercaptan)oate
26.59	Methyl (C18 Monoene monomercaptan)oate
26.66	Methyl (C18 Monoene monomercaptan)oate
26.80	Methyl (C18 monomercaptan)oate
27.31	Methyl (C18 cyclic sulfide)oate
27.44	Methyl (C18 cyclic sulfide)oate
29.04	Methyl (C18 dimercaptan)oate
29.15	Methyl (C18 dimercaptan)oate
29.37	Methyl (C18 monoene dimercaptan)oate
29.46	Methyl (C18 monoene dimercaptan)oate
30.50	Methyl (C18 di (cyclic sulfide))oate

Peaks at 29.37 or 29.46 could also contain Methyl (C18 cyclic sulfide monomercaptan)oate isomers as part of those peaks.

DETD FIG. 5 provides a GC/MS trace of an epoxidized soybean oil contacted with hydrogen sulfide (a hydroxy \*\*\*thiol\*\*\* containing ester)

subjected to the methanolysis procedure and analyzed by GC/MS using a HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 13 provides the GC/MS trace peak assignments.

TABLE 13

GC/MS Data for Methanolysis of a Hydroxy \*\*\*Thiol\*\*\* Containing Ester Produced from Epoxidized Soybean Oil  
GC Retention time Methyl Ester Carboxylic Acid Assignment

16.09	Methyl hexadecanoate
17.68	Methyl octadecanoate
18.94	Methyl (C18 monoepoxide)ate
19.94	Methyl (C18 diepoxide)ate
20.14	Methyl (C18 diepoxide)ate
20.75	Methyl (C18 monohydroxy monothiol)ate
21-21.5	Methyl (C18 triepoxide)ate
22.82	Methyl (C18 dihydroxy dithiol)ate
22.90	Methyl (C18 monoepoxide monohydroxy monothiol)ate

27-27.5 Unidentified mixture of C18 sulfur containing methyl esters

DETD The methanolysis procedure and GC/MS procedure has been illustrate using soybean oil, epoxidized soybean oil, and the \*\*\*thiol\*\*\* containing products derived from soybean oil and epoxidized soybean oil.

However, one skilled in the art can easily adapt the procedures to the analysis of other unsaturated esters, epoxidized unsaturated ester, and the \*\*\*thiol\*\*\* containing products derived from the unsaturated

esters and epoxidized unsaturated esters as described herein.

DETD The polythiourethane produced from the \*\*\*thiol\*\*\* containing

esters, hydroxy \*\*\*thiol\*\*\* containing esters, and cross linked

\*\*\*thiol\*\*\* containing ester were analyzed using ASTM E1545-95A and

E228-95 to provide the glass transition temperatures and the coefficients of thermal expansion. Shore hardness of the polythiourethanes were determined using ASTM D2240-02A. The polythiourethane were also subject to a subjective analysis classifying

the polythiourethanes as hard, flexible, rubbery, rigid, tough, brittle, and other characteristics.

CLM What is claimed is:

1. A \*\*\*thiol\*\*\* ester composition comprising \*\*\*thiol\*\*\* ester

molecules having an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule, having an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule, and

having a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

CLM What is claimed is:  
 2. The \*\*\*thiol\*\*\* ester composition of claim 1, wherein the  
 \*\*\*thiol\*\*\* ester molecules have a molar ratio of cyclic  
 sulfides to  
 \*\*\*thiol\*\*\* groups ranging from 0 to 1.0.

CLM What is claimed is:  
 3. The \*\*\*thiol\*\*\* ester composition of claim 1, wherein the  
 \*\*\*thiol\*\*\* ester molecules have an average ranging from 1.5  
 to 9  
 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

CLM What is claimed is:  
 4. The \*\*\*thiol\*\*\* ester composition of claim 1, wherein the  
 \*\*\*thiol\*\*\* ester molecules have a molar ratio of carbon-  
 carbon double  
 bonds to \*\*\*thiol\*\*\* groups of less than 1.5.

CLM What is claimed is:  
 5. The \*\*\*thiol\*\*\* ester composition of claim 1, wherein the  
 \*\*\*thiol\*\*\* ester molecules have an average of greater than 2  
 weight  
 percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:  
 6. The \*\*\*thiol\*\*\* ester composition of claim 1, wherein  
 \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to  
 10  
 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:  
 7. The \*\*\*thiol\*\*\* ester composition of claim 1, wherein the  
 \*\*\*thiol\*\*\* ester molecules have an average of less than 30  
 mole  
 percent total sulfur present as cyclic sulfides.

CLM What is claimed is:  
 8. The \*\*\*thiol\*\*\* ester composition of claim 1, wherein the  
 \*\*\*thiol\*\*\* ester molecules have an average of less than 10  
 mole  
 percent total sulfur present as cyclic sulfides.

CLM What is claimed is:  
 9. The \*\*\*thiol\*\*\* ester composition of claim 1, wherein  
 greater  
 than 40 percent of \*\*\*thiol\*\*\* ester molecule total side  
 chains  
 contain sulfur.

CLM What is claimed is:  
 10. A process for producing a \*\*\*thiol\*\*\* ester composition  
 comprising the steps of: a) contacting hydrogen sulfide and an  
 unsaturated ester composition comprising unsaturated esters  
 having an  
 average of at least 1.5 ester groups per unsaturated ester  
 molecule and  
 having an average of at least 1.5 carbon-carbon double bonds per  
 unsaturated ester molecule; and b) reacting the hydrogen sulfide  
 and

the unsaturated esters to form a \*\*\*thiol\*\*\* ester composition comprising \*\*\*thiol\*\*\* ester molecules having a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

CLM What is claimed is:  
15. The process of claim 10, wherein the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds of greater than 2.

CLM What is claimed is:  
18. The process of claim 10, wherein the \*\*\*thiol\*\*\* ester molecules have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:  
20. The process of claim 10, wherein greater than 40 percent of the \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur.

CLM What is claimed is:  
22. A process for producing a \*\*\*thiol\*\*\* ester composition comprising the steps of: a) contacting hydrogen sulfide and an unsaturated ester composition comprising unsaturated esters having an average of at least 1.5 ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule; and b) reacting the hydrogen sulfide and the unsaturated esters in a substantial absence of a solvent to form the \*\*\*thiol\*\*\* ester composition comprising \*\*\*thiol\*\*\* ester molecules.

CLM What is claimed is:  
25. The process of claim 22, wherein the \*\*\*thiol\*\*\* ester molecules have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

CLM What is claimed is:  
26. The process of claim 22, wherein the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds is greater than 1.

CLM What is claimed is:  
29. The process of claim 22, wherein the \*\*\*thiol\*\*\* ester molecules have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:  
 31. The process of claim 22, wherein greater than 40 percent of the  
 the \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur.

CLM What is claimed is:  
 32. A process for preparing a \*\*\*thiol\*\*\* ester composition  
 comprising: a) contacting a polyol composition and a  
 \*\*\*thiol\*\*\*  
 carboxylic acid composition; and b) reacting the polyol  
 composition and  
 the \*\*\*thiol\*\*\* carboxylic acid composition to produce the  
 \*\*\*thiol\*\*\* ester composition comprising \*\*\*thiol\*\*\*  
 ester  
 molecules having an average of at least 1.5 ester groups per  
 \*\*\*thiol\*\*\* ester molecule and having an average of at least  
 1.5  
 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

IT 102-85-2, Tri-n-butylphosphite \*\*\*6674-22-2\*\*\* ,  
 1,8-Diazabicyclo[5.4.0]undec-7-ene  
 (activator; thiol ester compns. prepd. by reacting H2S with  
 unsatd.  
 esters, such as soybean oil for manuf. monomers for prodn. of  
 polythiourethanes for fertilizers)

L7 ANSWER 31 OF 60 USPATFULL on STN  
 ACCESSION NUMBER: 2005:227538 USPATFULL <<LOGINID:20091205>>  
 TITLE: \*\*\*Thiol\*\*\* ester compositions and processes  
 for  
 making and using same  
 INVENTOR(S): Byers, Jim D., Bartlesville, OK, UNITED STATES  
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 DEPARTMENT -  
 IP, P.O BOX 4910, THE WOODLANDS, TX, 77387-4910,  
 US  
 NUMBER OF CLAIMS: 18  
 EXEMPLARY CLAIM: 1  
 NUMBER OF DRAWINGS: 14 Drawing Page(s)  
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 CAS INDEXING IS AVAILABLE FOR THIS PATENT.



TI        \*\*\*thiol\*\*\*    ester compositions and processes for making and  
 using  
          same  
 AB        \*\*\*thiol\*\*\*    ester compositions, methods of making the  
 \*\*\*thiol\*\*\*  
          ester compositions, and methods of using the    \*\*\*thiol\*\*\*  
 ester  
          compositions are provided. In some embodiments, the    \*\*\*thiol\*\*\*  
          ester compositions include    \*\*\*thiol\*\*\*    esters, hydroxy  
 \*\*\*thiol\*\*\*  
          esters and cross-linked    \*\*\*thiol\*\*\*    esters. The    \*\*\*thiol\*\*\*  
          ester composition can be used to produce cross-linked  
 \*\*\*thiol\*\*\*  
          esters, sulfonic acid-containing esters, sulfonate containing  
 esters and  
          thioacrylate containing esters. The    \*\*\*thiol\*\*\*    ester  
 compositions  
          can be used to produce polythiourethanes. The polythiourethanes  
 can be  
          used in fertilizers and fertilizer coatings.  
 SUMM    The invention relates to    \*\*\*thiol\*\*\*    containing ester  
 compositions  
          generally made from a reaction of unsaturated ester compositions  
 and a  
          material capable of forming a    \*\*\*thiol\*\*\*    group. The  
 invention also  
          relates to the processes for preparing such    \*\*\*thiol\*\*\*  
 containing  
          compositions and uses for the    \*\*\*thiol\*\*\*    containing  
 compositions.

SUMM    The present invention advantageously provides    \*\*\*thiol\*\*\*  
 containing compositions and methods of making such compositions.  
 In  
          addition to the compositions and methods of making such  
 compositions,  
          products that include such compositions are also provided.

SUMM    As an embodiment of the present invention, a    \*\*\*thiol\*\*\*  
 ester  
          composition is advantageously provided. In this embodiment, the  
          \*\*\*thiol\*\*\*    ester composition includes    \*\*\*thiol\*\*\*    ester  
 molecules  
          that have an average of at least 1.5 ester groups per  
 \*\*\*thiol\*\*\*  
          ester molecule. The    \*\*\*thiol\*\*\*    ester molecules also have an  
 average  
          of at least 1.5    \*\*\*thiol\*\*\*    groups per    \*\*\*thiol\*\*\*    ester  
          molecule. The    \*\*\*thiol\*\*\*    ester molecules also have a molar  
 ratio of  
          cyclic sulfides to    \*\*\*thiol\*\*\*    groups of less than 1.5.

SUMM    In some aspects, the    \*\*\*thiol\*\*\*    ester molecules have a  
 molar ratio  
          of cyclic sulfides to    \*\*\*thiol\*\*\*    groups ranging from 0 to  
 1.0. In  
          some aspects, the    \*\*\*thiol\*\*\*    ester molecules have an average  
          ranging from 1.5 to 9    \*\*\*thiol\*\*\*    groups per    \*\*\*thiol\*\*\*  
 ester  
          molecule. In some embodiments, the    \*\*\*thiol\*\*\*    ester

molecules have  
a molar ratio of carbon-carbon double bonds to **\*\*\*thiol\*\*\***  
groups of  
less than 1.5.

SUMM The amount of **\*\*\*thiol\*\*\*** sulfur or **\*\*\*mercaptan\*\*\***  
sulfur  
contained within the **\*\*\*thiol\*\*\*** ester molecules can also  
vary. For  
example, in some embodiments, the **\*\*\*thiol\*\*\*** ester molecules  
have  
an average of greater than 5 weight percent **\*\*\*thiol\*\*\***  
sulfur. In  
other embodiments, the **\*\*\*thiol\*\*\*** ester molecules have an  
average  
ranging from 8 to 10 weight percent **\*\*\*thiol\*\*\*** sulfur. In  
some  
embodiments, the **\*\*\*thiol\*\*\*** ester molecules have an average  
of less  
than 30 mole percent sulfur, which is present as cyclic sulfides.  
Alternatively, the **\*\*\*thiol\*\*\*** ester molecules have an  
average of  
less than 2 mole percent sulfur present as cyclic sulfides.

SUMM In some embodiments, the **\*\*\*thiol\*\*\*** ester molecules are  
produced  
from unsaturated esters that have an average of less than 25  
weight  
percent of side chains that include 3 contiguous methylene  
interrupted  
carbon-carbon double bonds. In another aspect, greater than 40  
percent  
of the total side chains contained within the **\*\*\*thiol\*\*\***  
ester  
molecules contain sulfur.

SUMM In addition to the **\*\*\*thiol\*\*\*** ester composition, a process  
for  
producing the **\*\*\*thiol\*\*\*** ester composition is advantageously  
provided as another embodiment of the present invention. To  
produce the  
**\*\*\*thiol\*\*\*** ester composition, hydrogen sulfide is contacted  
with an  
unsaturated ester composition. The unsaturated ester composition  
includes unsaturated esters that have an average of at least 1.5  
ester  
groups per unsaturated ester molecule. The unsaturated esters  
also have  
an average of at least 1.5 carbon-carbon double bonds per  
unsaturated  
ester molecule. The hydrogen sulfide and the unsaturated esters  
are  
reacted to produce or form the **\*\*\*thiol\*\*\*** ester composition.  
The  
**\*\*\*thiol\*\*\*** ester composition advantageously includes  
**\*\*\*thiol\*\*\***  
ester molecules that have a molar ratio of cyclic sulfides to  
**\*\*\*thiol\*\*\*** groups of less than 1.5.

SUMM Another process for producing the **\*\*\*thiol\*\*\*** ester

composition is advantageously provided as another embodiment of the present invention. In this process embodiment, the hydrogen sulfide and the unsaturated ester composition are contacted. The unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are then reacted in a substantial absence of a solvent to form the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules. The \*\*\*thiol\*\*\* ester composition advantageously includes \*\*\*thiol\*\*\* ester molecules that have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM The resulting \*\*\*thiol\*\*\* ester molecules produced by this process possess advantageous characteristics. For example, in some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds of greater than 2. As another example, in other embodiments, the \*\*\*thiol\*\*\* ester molecules have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. In some aspects, greater than 40 percent of the \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur.

SUMM As another embodiment of the present invention, another process for preparing the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, a polyol composition and a \*\*\*thiol\*\*\* carboxylic acid composition are contacted and reacted to produce the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules having an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

SUMM In addition to the \*\*\*thiol\*\*\* ester composition, other compositions are advantageously provided as embodiments of the present

invention. For example, a hydroxy \*\*\*thiol\*\*\* ester composition is provided as another embodiment of the present invention. The hydroxyl \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at least 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

SUMM As described herein, the .alpha.-hydroxy \*\*\*thiol\*\*\* groups contain an alcohol or hydroxy group and a \*\*\*thiol\*\*\* group within the same group. In embodiments of the present invention, the .alpha.-hydroxy \*\*\*thiol\*\*\* groups can be replaced with separate alcohol and \*\*\*thiol\*\*\* groups. In these embodiments, the same number of .alpha.-hydroxy groups can be used for the separate alcohol and \*\*\*thiol\*\*\* groups. For example, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups. In embodiments that contain separate alcohol and \*\*\*thiol\*\*\* groups, the hydroxy \*\*\*thiol\*\*\* ester molecules would contain an average of at least 1.5 alcohol groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups.

SUMM In some aspects, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 1.5 to 9 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM In some embodiments, the \*\*\*thiol\*\*\* ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the .alpha.-hydroxy \*\*\*thiol\*\*\* ester molecules contain sulfur.

SUMM The amount of \*\*\*thiol\*\*\* sulfur contained within the hydroxy \*\*\*thiol\*\*\* ester molecules can also vary. For example, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average

of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

SUMM In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have a molar ratio of \*\*\*epoxide\*\*\* groups to the .alpha.-hydroxy \*\*\*thiol\*\*\* groups of less than 2. In other aspects, the composition is substantially free of \*\*\*epoxide\*\*\* groups.

SUMM In addition to the hydroxy \*\*\*thiol\*\*\* ester composition, methods or processes for making the hydroxy \*\*\*thiol\*\*\* ester composition are advantageously provided as embodiments of the present invention. In an embodiment, a process for preparing the hydroxy \*\*\*thiol\*\*\* ester composition is provided that includes the step of contacting the hydrogen sulfide and an epoxidized unsaturated ester composition. The epoxidized unsaturated ester composition includes epoxidized esters having an average of at least 1.5 ester groups per epoxidized unsaturated ester molecule and having an average of at least 1.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. The hydrogen sulfide and the epoxidized unsaturated esters are then reacted to form the hydroxy \*\*\*thiol\*\*\* ester composition.

SUMM In some embodiments, a molar ratio of the hydrogen sulfide to \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated esters is greater than 1.

SUMM Another process for preparing the hydroxy \*\*\*thiol\*\*\* ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, a polyol composition and a hydroxy \*\*\*thiol\*\*\* carboxylic acid composition are contacted and reacted to produce the hydroxy \*\*\*thiol\*\*\* ester composition. In this embodiment, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at least 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

SUMM A cross-linked \*\*\*thiol\*\*\* ester composition is advantageously

provided as another embodiment of the present invention. The cross-linked \*\*\*thiol\*\*\* ester composition includes

\*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q-- , wherein Q is greater than 1. In some embodiments, the \*\*\*thiol\*\*\* ester oligomers have at least three \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages. In another aspect, the \*\*\*thiol\*\*\* ester oligomers have from 3 to 20 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

SUMM In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition includes both \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers. In some embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content ranging from 0.5 to 8 weight percent; or alternatively, ranging from 8 to 15 weight percent. The combined \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers can have an average molecular weight greater than 2000; or alternatively, in a range from 2000 to 20,000.

SUMM As another embodiment of the present invention, a cross-linked \*\*\*thiol\*\*\* ester composition produced by the process comprising the steps of contacting the \*\*\*thiol\*\*\* ester composition with an oxidizing agent and reacting the \*\*\*thiol\*\*\* ester and the oxidizing agent to form \*\*\*thiol\*\*\* ester oligomers is advantageously provided. In this embodiment, the \*\*\*thiol\*\*\* ester oligomers have at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q-- , wherein Q is greater than 1.

SUMM A process to produce the cross-linked \*\*\*thiol\*\*\* ester composition is also advantageously provided as another embodiment of the present invention. In this process, a \*\*\*thiol\*\*\* ester composition is contacted and reacted with an oxidizing agent to form \*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q-- , wherein Q is greater than 1. In some embodiments, the oxidizing agent is

elemental sulfur, oxygen, or hydrogen peroxide. In an aspect, the oxidizing agent is elemental sulfur.

SUMM In an aspect, the \*\*\*thiol\*\*\* ester is a hydroxy  
\*\*\*thiol\*\*\*  
ester. In other aspects, a weight ratio of elemental sulfur to  
\*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester molecules  
ranges from  
0.5 to 32.

SUMM The step of the reacting the \*\*\*thiol\*\*\* ester and the  
oxidizing  
agent can be performed at a temperature ranging from 25.degree.  
C. to  
150.degree. C. The process for producing the cross-linked  
\*\*\*thiol\*\*\*  
ester composition can also include the step of stripping residual  
hydrogen sulfide from the cross-linked \*\*\*thiol\*\*\* ester  
composition  
produced. In another aspect, the reaction of the \*\*\*thiol\*\*\*  
ester  
and the elemental sulfur is catalyzed. In some embodiments, the  
catalyst  
is an amine.

SUMM In another of its aspects, the present invention relates to a  
controlled release fertilizer material comprising a particulate  
plant  
nutrient surrounded by a coating which is the reaction product of  
a  
mixture comprising: (i) a first component selected from an  
isocyanate  
and/or an epoxy resin, and (ii) a first active hydrogen-  
containing  
compound selected from the group consisting of a \*\*\*thiol\*\*\*  
ester  
composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a  
cross-linked  
\*\*\*thiol\*\*\* ester composition and mixtures thereof.

SUMM In another of its aspects, the present invention relates to a  
process  
for the production of abrasion resistant polythiourethane and/or  
epoxy  
polymer encapsulated controlled release fertilizer particles by  
incorporating in urethane and/or epoxy polymer forming reaction  
mixture  
a sulfur-containing compound such as one or more of a  
\*\*\*thiol\*\*\*  
ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a  
cross-linked \*\*\*thiol\*\*\* ester composition, other sulfur-  
based  
compounds described herein below and mixtures thereof.

SUMM Preferably, for the production of the present polythiourethane  
encapsulated controlled release fertilizer material, a sulfur-  
containing  
compound (e.g., one or more of a \*\*\*thiol\*\*\* ester  
composition; a  
hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked

\*\*\*thiol\*\*\*  
ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil. In one preferred embodiment, the sulfur-containing vegetable oil comprises a mercaptanized vegetable oil (MVO), more preferably as described in more detail herein, even more preferably an MVO produced by the addition of hydrogen sulfide to a vegetable oil. In another preferred embodiment, the sulfur-containing vegetable oil comprises mercapto-hydroxy vegetable oil (MHVO), more preferably as described in more detail herein, even more preferably an MHVO produced by the addition of hydrogen sulfide to epoxidized vegetable oil. In yet another preferred embodiment, the sulfur-containing vegetable oil comprises sulfur cross-linked mercaptanized vegetable oil (CMVO), more preferably as described in more detail herein, even more preferably an CMVO produced by the addition of elemental sulfur to mercaptanized vegetable oil (MVO).

SUMM Preferably, for the production of epoxy polymer encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a \*\*\*thiol\*\*\* ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil (e.g., MVO and/or MHVO and/or CMVO) is used as one of the epoxy resin-reactive components.

DRWD FIG. 1 includes two graphs that compare the NMR's of soybean oil, which is shown in the top graph, and a \*\*\*thiol\*\*\* containing ester produced from soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 2 includes two graphs that compare the NMR's of epoxidized soybean oil, which is shown in the top graph, and a \*\*\*thiol\*\*\* containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 3 is a gas chromatograph (GC)/mass spectrometer (MS) trace of a \*\*\*thiol\*\*\* containing ester that was produced from soybean oil in accordance with an embodiment of the present invention and then



treated by methanolysis;  
DRWD FIG. 5 is a GC/MS trace of hydroxy \*\*\*thiol\*\*\* containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention and then treated by methanolysis;  
DETD In this specification, " \*\*\*thiol\*\*\* ester composition" refers to an ester composition that includes " \*\*\*thiol\*\*\* ester molecules." The \*\*\*thiol\*\*\* ester molecule has at least one \*\*\*thiol\*\*\* group and at least one ester group within the \*\*\*thiol\*\*\* ester molecule.  
DETD In this specification, "hydroxy \*\*\*thiol\*\*\* ester composition" refers to an ester composition that includes "hydroxy \*\*\*thiol\*\*\* ester molecules." The hydroxy \*\*\*thiol\*\*\* ester molecule has at least one \*\*\*thiol\*\*\* group, at least one ester group, and at least one hydroxy or alcohol group within the hydroxy \*\*\*thiol\*\*\* ester molecule. Alternatively, the alcohol group and the \*\*\*thiol\*\*\* group can be combined in the same group, which is referred to as an ".alpha.-hydroxy \*\*\*thiol\*\*\* group."  
DETD In this specification, "polythiourethane" refers to a urethane composition that includes more than one of the following structure:  
##STR1## The presence of the thiourethane group can be determined by method known to those skilled in the art (for example infrared spectroscopy, Raman spectroscopy, and/or NMR). \*\*\*Thiol\*\*\*  
Ester Composition  
DETD The present invention advantageously provides a \*\*\*thiol\*\*\* ester composition as an embodiment of the present invention. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule. The \*\*\*thiol\*\*\* ester composition also has a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5, as described herein.  
DETD Generally, the \*\*\*thiol\*\*\* ester composition contains molecules having at least one ester group and at least one \*\*\*thiol\*\*\* group. The \*\*\*thiol\*\*\* ester composition of this invention can be produced from any unsaturated ester, as described herein. Because the feedstock unsaturated esters can contain multiple carbon-carbon double

bonds per unsaturated ester molecule, carbon-carbon double bond reactivity and statistical probability dictate that each \*\*\*thiol\*\*\* ester molecule of the \*\*\*thiol\*\*\* ester composition produced from the unsaturated ester composition will not have the same number of \*\*\*thiol\*\*\* groups, number of unreacted carbon-carbon double bonds, number of cyclic sulfides, molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* groups, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups and other quantities of functional groups and molar ratios disclosed herein as the feedstock unsaturated ester. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Thus, many of these properties will be discussed as an average number of the groups per \*\*\*thiol\*\*\* ester molecule within the \*\*\*thiol\*\*\* ester composition or average ratio per \*\*\*thiol\*\*\* ester molecule within the \*\*\*thiol\*\*\* ester composition. In other embodiments, it is desired to control the content of \*\*\*thiol\*\*\* sulfur present in the \*\*\*thiol\*\*\* ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every carbon-carbon double bond within the unsaturated ester, certain molecules of \*\*\*thiol\*\*\* ester can have more or less \*\*\*thiol\*\*\* groups than other molecules. Thus, the weight percent of \*\*\*thiol\*\*\* groups is stated as an average across all \*\*\*thiol\*\*\* ester molecules of the \*\*\*thiol\*\*\* ester composition.

DETD The \*\*\*thiol\*\*\* ester can be derived from any unsaturated ester described herein.

DETD The \*\*\*thiol\*\*\* ester compositions can be described as comprising one or more separate or discreet functional groups of the \*\*\*thiol\*\*\* ester molecule and/or \*\*\*thiol\*\*\* ester composition. These independent functional groups can include: the number of (or average number of) ester groups per \*\*\*thiol\*\*\* ester molecule, \*\*\*thiol\*\*\* containing the number of (or average number of) \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule, the number of (or average number of) unreacted carbon-carbon double bonds per \*\*\*thiol\*\*\* ester molecule, the average \*\*\*thiol\*\*\*

sulfur content of the \*\*\*thiol\*\*\* ester composition, the percentage (or average percentage) of sulfide linkages per \*\*\*thiol\*\*\* ester molecule, and the percentage (or average percentage) of cyclic sulfide groups per \*\*\*thiol\*\*\* ester molecule. Additionally, the \*\*\*thiol\*\*\* ester compositions can be described using individual or a combination of ratios including the ratio of double bonds to \*\*\*thiol\*\*\* groups, the ratio of cyclic sulfides to \*\*\*mercaptan\*\*\* group, and the like.

As separate elements, these functional groups of the \*\*\*thiol\*\*\* composition will be described separately.

DETD Minimally, in some embodiments, the \*\*\*thiol\*\*\* ester contains \*\*\*thiol\*\*\* ester molecules having at least one ester group and one \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester molecule. As the \*\*\*thiol\*\*\* ester is prepared from unsaturated esters, the \*\*\*thiol\*\*\* ester can contain the same number of ester groups as the unsaturated esters described herein. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule. Alternatively, the \*\*\*thiol\*\*\* ester molecules have an average of at least 2 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 ester groups per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 ester groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments, the \*\*\*thiol\*\*\* esters have an average of from 1.5 to 8 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 7 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2.5 to 5 ester groups per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 3 to 4 ester groups per \*\*\*thiol\*\*\* ester molecule. In yet other embodiments, the \*\*\*thiol\*\*\* ester comprises an average of 3 ester groups per \*\*\*thiol\*\*\* ester molecule or alternatively, an average of 4 ester groups per unsaturated ester molecule.

DETD Minimally, the \*\*\*thiol\*\*\* ester comprises an average of at least one \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester molecule. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester

molecule;  
alternatively, \*\*\*thiol\*\*\* containing an average of at least  
2 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule;  
alternatively,  
an average of at least 2.5 \*\*\*thiol\*\*\* groups per  
\*\*\*thiol\*\*\*  
ester molecule; or alternatively, an average of at least 3  
\*\*\*thiol\*\*\*  
groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments,  
the \*\*\*thiol\*\*\* ester molecules have an average of from 1.5 to 9  
\*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule;  
alternatively,  
an average of from 3 to 8 \*\*\*thiol\*\*\* groups per  
\*\*\*thiol\*\*\*  
ester molecule; alternatively, \*\*\*thiol\*\*\* containing an  
average of  
from 2 to 4 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester  
molecule,  
or alternatively, an average of from 4 to 8 \*\*\*thiol\*\*\*  
groups per  
\*\*\*thiol\*\*\* ester molecule.  
DETD In other embodiments, the \*\*\*thiol\*\*\* ester can be described  
by the  
average amount of \*\*\*thiol\*\*\* sulfur present in \*\*\*thiol\*\*\*  
ester. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have  
an  
average of at least 5 weight percent \*\*\*thiol\*\*\* sulfur per  
\*\*\*thiol\*\*\* ester molecule; alternatively, an average of at  
least 10  
weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester  
molecule, or alternatively, an average of greater than 15 weight  
percent  
\*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule. In an  
embodiment, the \*\*\*thiol\*\*\* ester molecules have an average  
of from  
5 to 25 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\*  
ester  
molecule; alternatively, an average of from 5 to 20 weight  
percent  
\*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule;  
alternatively,  
an average of from 6 to 15 weight percent \*\*\*thiol\*\*\* sulfur  
per  
\*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
from 8 to  
10 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\*  
ester  
molecule.  
DETD Generally, the location of the \*\*\*thiol\*\*\* group of the  
\*\*\*thiol\*\*\* ester is not particularly important and will be  
dictated  
by the method used to produce the \*\*\*thiol\*\*\* ester. In  
embodiments  
wherein the \*\*\*thiol\*\*\* ester is produced by contacting an  
unsaturated ester, the position of the \*\*\*thiol\*\*\* group will  
be  
dictated by the position of the carbon-carbon double bond. When  
the

carbon-carbon double bond is an internal carbon-carbon double bond, the method of producing the \*\*\*thiol\*\*\* ester will result in a secondary \*\*\*thiol\*\*\* group. However, when the double bond is located at a terminal position it is possible to choose reaction conditions to produce a \*\*\*thiol\*\*\* ester comprising either a primary \*\*\*thiol\*\*\* group or a secondary \*\*\*thiol\*\*\* group.

DETD Some methods of producing the \*\*\*thiol\*\*\* ester composition can additionally create sulfur containing functional groups other than a \*\*\*thiol\*\*\* group. For example, in some \*\*\*thiol\*\*\* ester production methods, an introduced \*\*\*thiol\*\*\* group can react with a carbon-carbon double bond within the same unsaturated ester to produce a sulfide linkage. When the reaction is with a double bond of a second unsaturated ester, this produces a simple sulfide linkage.

However, in some instances, the second carbon-carbon double bond is located in the same unsaturated ester molecule. When the \*\*\*thiol\*\*\* group reacts with a second carbon-carbon double bond within the same unsaturated ester molecule, a sulfide linkage is produced. In some instances, the carbon-carbon double bond can be within a second ester group of the unsaturated ester molecule. While in other instances, the carbon-carbon double bond can be within the same ester group of the unsaturated ester molecule.

DETD When the \*\*\*thiol\*\*\* group reacts with the carbon-carbon double bond in a second ester group of the same unsaturated ester molecule, the cyclic sulfide would contain two ester groups contained within a ring structure. When the \*\*\*thiol\*\*\* group reacts with the carbon-carbon double bond within the same ester group, the cyclic sulfide would not contain an ester group within the ring structure. Within this specification, this second type of cyclic sulfide is referred to as a cyclic sulfide. Within this specification, the first type of cyclic sulfide is referred to as a simple sulfide. In the cyclic sulfide case, the sulfide linkage produces a cyclic sulfide functionality within a single ester group of the \*\*\*thiol\*\*\* ester. This linkage is termed a cyclic sulfide for purposes of this application. One such sulfide

group that can be produced is a cyclic sulfide. The cyclic sulfide rings that can be produced include a tetrahydrothiopyran ring, a thietane ring, or a thiophane ring (tetrahydrothiophene ring).

DETD In some embodiments, it is desirable to control the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* ester. In an embodiment the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* ester molecules comprises less than 30 mole percent.

Alternatively, the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* esters comprises less than 20 mole percent; alternatively, less than 10 mole percent; alternatively, less than 5 mole percent; or alternatively, less than 2 mole percent. In other embodiments, it is desired to control the molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups. In other embodiments, it is desirable to have molar ratios of cyclic sulfide to \*\*\*thiol\*\*\* group. In an embodiment, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester is less than 1.5. Alternatively, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester is less than 1; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, 0.1. In some embodiments, the ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester ranges from 0 to 1; or alternatively, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester ranges between 0.05 and 1.

DETD In some instances it can be desirable to have carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester composition while in other embodiments it can be desirable to minimize the number of carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester composition.

The presence of carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester can be stated as an average molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* -sulfur. In an embodiment, the average ratio of the remaining unreacted carbon-carbon double bond in the \*\*\*thiol\*\*\* ester composition to \*\*\*thiol\*\*\* sulfur is less than 1.5 per \*\*\*thiol\*\*\* ester molecule. Alternatively, the average ratio of carbon-carbon double bond to \*\*\*thiol\*\*\* sulfur is less than 1.2 per

\*\*\*\*thiol\*\*\* ester molecule; alternatively, less than 1.0 per  
 \*\*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.75 per  
 \*\*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.5 per  
 \*\*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.2 per  
 \*\*\*\*thiol\*\*\* ester molecule; or alternatively, less than 0.1

per  
 \*\*\*\*thiol\*\*\* ester molecule.

DETD In particular embodiments, the \*\*\*\*thiol\*\*\* ester is produced  
 from unsaturated ester compositions. Because the feedstock unsaturated  
 ester has particular compositions having a certain number of ester  
 groups present, the product \*\*\*\*thiol\*\*\* ester composition will have  
 about the same number of ester groups per \*\*\*\*thiol\*\*\* ester  
 molecule as the feedstock unsaturated ester. Other, independent \*\*\*\*thiol\*\*\*  
 ester properties described herein can be used to further describe  
 the \*\*\*\*thiol\*\*\* ester composition.

DETD In some embodiments, the \*\*\*\*thiol\*\*\* ester molecules are  
 produced from unsaturated esters having an average of less than 25 weight  
 percent of side chains having 3 contiguous methylene interrupted carbon-  
 carbon double bonds, as described herein. In some embodiments, greater  
 than 40 percent of the \*\*\*\*thiol\*\*\* containing natural source total  
 side chains can include sulfur. In some embodiments, greater than 60  
 percent of the \*\*\*\*thiol\*\*\* ester molecule total side chains can  
 include sulfur. In other embodiments, greater than 50, 70, or 80 percent  
 of the \*\*\*\*thiol\*\*\* ester molecule total side chains can include  
 sulfur.

DETD In an embodiment, the \*\*\*\*thiol\*\*\* ester is a \*\*\*\*thiol\*\*\*  
 containing natural source oil, as described herein. When the  
 \*\*\*\*thiol\*\*\* ester is a \*\*\*\*thiol\*\*\* containing natural  
 source oil,  
 functional groups that are present in the \*\*\*\*thiol\*\*\*  
 containing natural source oil can be described in a "per \*\*\*\*thiol\*\*\*  
 ester molecule" basis or in a "per triglyceride" basis. The  
 \*\*\*\*thiol\*\*\*  
 containing natural source oil can have substantially the same  
 properties as the \*\*\*\*thiol\*\*\* ester composition, such as the molar  
 ratios and other independent descriptive elements described herein.

DETD The average number of \*\*\*\*thiol\*\*\* groups per triglyceride in  
 the \*\*\*\*thiol\*\*\* containing natural source oil is greater than  
 about 1.5.

In some embodiments, the average number of \*\*\*\*thiol\*\*\* groups  
 per

triglyceride can range from about 1.5 to about 9.  
 DETD The \*\*\*thiol\*\*\* ester compositions can also be described as  
 a product produced by the process comprising contacting hydrogen  
 sulfide and an unsaturated ester composition and can be further limited  
 by the process as described herein. The \*\*\*thiol\*\*\* containing  
 natural source oil can also be described using a molecular weight or an  
 average molecular weight of the side chains.  
 DETD Hydroxy \*\*\*Thiol\*\*\* Ester Composition  
 DETD In embodiments of the present invention, the \*\*\*thiol\*\*\*  
 ester compositions can also contain a hydroxy or alcohol group. When  
 the \*\*\*thiol\*\*\* ester composition includes the hydroxy group, the  
 hydroxy \*\*\*thiol\*\*\* ester composition is referred to herein as the  
 alcohol \*\*\*thiol\*\*\* ester composition. The quantity or number of  
 groups present in the hydroxy \*\*\*thiol\*\*\* ester composition  
 can be independent of the quantity of other functional groups present in  
 the hydroxy \*\*\*thiol\*\*\* ester composition (i.e. \*\*\*thiol\*\*\*  
 groups, ester groups, sulfides, cyclic sulfides). Additionally, the  
 weight percent of \*\*\*thiol\*\*\* sulfur and functional group ratios  
 (i.e. molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups, molar  
 ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, molar ratio  
 of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\*  
 groups and other disclosed quantities of functional groups and their molar  
 ratios to the \*\*\*thiol\*\*\* groups) are separate or discreet elements  
 that can be used to describe the hydroxy \*\*\*thiol\*\*\* ester  
 composition. The hydroxy \*\*\*thiol\*\*\* ester composition can be described  
 using any combination of the hydroxy \*\*\*thiol\*\*\* ester composition  
 separate functional groups or ratios described herein.  
 DETD In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester composition  
 is produced by reacting hydrogen sulfide with an epoxidized  
 unsaturated ester composition as described herein. Because the epoxidized  
 unsaturated ester can contain multiple \*\*\*epoxide\*\*\* groups,  
 \*\*\*epoxide\*\*\* group reactivity and statistical probability  
 dictate that not all hydroxy \*\*\*thiol\*\*\* ester molecules of the  
 hydroxy \*\*\*thiol\*\*\* ester composition will have the same number of



hydroxy groups, \*\*\*thiol\*\*\* groups, .alpha.-hydroxy \*\*\*thiol\*\*\* groups, sulfides, cyclic sulfides, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups, weight percent \*\*\*thiol\*\*\* sulfur and other disclosed quantities of functional groups and their molar ratios as the epoxidized unsaturated ester composition. Thus, many of these properties will be discussed as an average number or ratio per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, it is desired to control the content of \*\*\*thiol\*\*\* sulfur present in the hydroxy \*\*\*thiol\*\*\* ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every \*\*\*epoxide\*\*\* group within the epoxidized unsaturated ester, certain hydroxy \*\*\*thiol\*\*\* ester molecules can have more or less \*\*\*thiol\*\*\* groups than other molecules within the hydroxy \*\*\*thiol\*\*\* ester composition. Thus, the weight percent of \*\*\*thiol\*\*\* groups can be stated as an average weight percent across all hydroxy \*\*\*thiol\*\*\* ester molecules. DETD As an embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1 ester groups and an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. As an embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester comprises at least one ester, at least one \*\*\*thiol\*\*\* group, and at least one hydroxy group. Because the hydroxy \*\*\*thiol\*\*\* ester is prepared from epoxidized unsaturated esters, the hydroxy \*\*\*thiol\*\*\* ester can contain the same number of ester groups as the epoxidized unsaturated esters. In an embodiment, the hydroxy \*\*\*thiol\*\*\*

ester molecules have an average of at least 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. Alternatively, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 2 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy \*\*\*thiol\*\*\* esters have an average of from 1.5 to 8 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 7 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2.5 to 5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 3 to 4 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In yet other embodiments, the .alpha.-hydroxy \*\*\*thiol\*\*\* ester comprises an average of 3 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule or alternatively, an average of 4 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD In some embodiments, the hydroxy group and the \*\*\*thiol\*\*\* group are combined in the same group, which produces the .alpha.-hydroxy \*\*\*thiol\*\*\* group. In other embodiments, the \*\*\*thiol\*\*\* group and the hydroxy or alcohol group are not in the same group. When this occurs, to produce the hydroxy \*\*\*thiol\*\*\* ester composition, the alcohol group is added independently of the \*\*\*thiol\*\*\* group. For example, as another embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition advantageously includes hydroxy \*\*\*thiol\*\*\* ester molecules. The hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 ester groups, an average of at least 1.5 \*\*\*thiol\*\*\* groups, and an average of at least 1.5 alcohol groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester comprises at least one \*\*\*thiol\*\*\* group per hydroxy \*\*\*thiol\*\*\* ester molecule. In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 \*\*\*thiol\*\*\* groups per

of at hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
 least 2 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule; alternatively, an average of at least 2.5 \*\*\*thiol\*\*\*  
 groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an  
 average of at least 3 \*\*\*thiol\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\*  
 ester molecule. In other embodiments, the hydroxy \*\*\*thiol\*\*\*  
 ester  
 molecules have an average of from 1.5 to 9 \*\*\*thiol\*\*\* groups  
 per  
 hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
 of  
 from 3 to 8 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\*  
 ester  
 molecule; alternatively, an average of from 2 to 4 \*\*\*thiol\*\*\*  
 groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an  
 average of from 4 to 8 \*\*\*thiol\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\*  
 ester.  
 DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\*  
 ester  
 composition comprises an average of at least 1 hydroxy or alcohol  
 group  
 per hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments,  
 the  
 hydroxy \*\*\*thiol\*\*\* ester composition comprises an average of  
 at  
 least 1.5 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule;  
 alternatively, average of at least 2 hydroxy groups per hydroxy  
 \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at  
 least 2.5  
 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an average of at least 3 hydroxy groups per  
 \*\*\*thiol\*\*\*  
 ester molecule. In other embodiments, the \*\*\*thiol\*\*\* ester  
 composition comprises an average of from 1.5 to 9 hydroxy groups  
 per  
 hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
 of  
 from 3 to 8 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule;  
 alternatively, an average of from 2 to 4 hydroxy groups per  
 hydroxy  
 \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
 from 4 to  
 8 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule.  
 DETD In yet other embodiments, the number of hydroxy groups can be  
 stated as  
 an average molar ratio of hydroxy group to \*\*\*thiol\*\*\*  
 groups.  
 Minimally, in some embodiments, the molar ratio of hydroxy groups  
 to  
 \*\*\*thiol\*\*\* groups is at least 0.25. In some embodiments, the  
 molar  
 ratio of hydroxy groups to \*\*\*thiol\*\*\* groups is at least  
 0.5;

alternatively, at least 0.75; alternatively, at least 1.0; alternatively, at least 1.25; or alternatively, at least 1.5. In other groups embodied, the molar ratio of hydroxy groups to \*\*\*thiol\*\*\* ranges from 0.25 to 2.0; alternatively, from 0.5 to 1.5; or alternatively, from 0.75 to 1.25.

DETD In embodiments where the hydroxy \*\*\*thiol\*\*\* esters are produced from an epoxidized unsaturated ester, the hydroxy \*\*\*thiol\*\*\* esters can be described as containing ester groups and .alpha.-hydroxy \*\*\*thiol\*\*\* groups. The number of ester groups and the number of .alpha.-hydroxy \*\*\*thiol\*\*\* groups are independent elements and as such the hydroxy \*\*\*thiol\*\*\* esters can be described as having any combination of ester groups and .alpha.-hydroxy \*\*\*thiol\*\*\* groups described herein. Minimally, the hydroxy \*\*\*thiol\*\*\* ester comprises an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* group per hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition comprises an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition comprises an average of from 1.5 to 9 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 3 to 8 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 4 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 4 to 8 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD The hydroxy \*\*\*thiol\*\*\* esters can be produced by contacting an epoxidized ester derived from an unsaturated ester (i.e., unsaturated ester), as described herein. In some instances it can be desirable to have \*\*\*epoxide\*\*\* groups present in the hydroxy

\*\*\*thiol\*\*\* ester composition. While in other embodiments, it can be desirable to minimize the number of epoxy groups present in the hydroxy

\*\*\*thiol\*\*\* ester composition. Thus, the presence of residual \*\*\*epoxide\*\*\* groups can be another separate functional group used to describe the hydroxy \*\*\*thiol\*\*\* ester.

DETD The presence of \*\*\*epoxide\*\*\* groups in the hydroxy \*\*\*thiol\*\*\* ester can be independently described as an average number of \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester, a molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, a molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups, or any combination thereof. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules comprise an average of less than 2 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule, i.e., the hydroxy \*\*\*thiol\*\*\* ester molecules have a molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups of less than 2. Alternatively, the hydroxy \*\*\*thiol\*\*\* ester comprises an average of less than 1.5 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of less than 1 \*\*\*epoxide\*\*\* group per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of less than 0.75 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of less than 0.5 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

In other embodiments, the molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups averages less than 1.5. Alternatively, the molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups averages less than 1; alternatively, averages less than 0.75; alternatively, averages less than 0.5; alternatively, averages less than 0.25; or alternatively, averages less than 0.1. In yet other embodiments, the molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups averages less than 1.5. Alternatively, the molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups averages less than 1; alternatively, averages less than 0.75; alternatively, averages less than 0.5; alternatively, averages less than 0.25; or alternatively, averages less than 0.1.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition is substantially free of \*\*\*epoxide\*\*\* groups.

DETD In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester can be described by the average amount of \*\*\*thiol\*\*\* sulfur present in hydroxy \*\*\*thiol\*\*\* ester. In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 2.5 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 5 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 10 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of greater than 15 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule. In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of from 5 to 25 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 5 to 20 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 6 to 15 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group. In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group. In some embodiments, at least 60 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group; alternatively, at least 70 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group. Yet in other embodiments, at least 80 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group.

DETD In some aspects, greater than 20 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur. In some aspects, greater than 40 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur. In some aspects, greater than 60 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains

contain sulfur; alternatively, greater than 70 percent of the total side chains contain sulfur; or alternatively, greater than 80 percent of the total side chains contain sulfur.

DETD In particular embodiments, the epoxidized unsaturated ester used in the synthesis of the hydroxy \*\*\*thiol\*\*\* ester is produced from the epoxidized unsaturated ester composition that includes an epoxidized natural source oil. Because the natural source oils have particular compositions regarding the number of ester groups present, the hydroxy \*\*\*thiol\*\*\* ester will have about the same number of ester groups as the feedstock natural source oil. Other independent properties that are described herein can be used to further describe the hydroxy \*\*\*thiol\*\*\* ester.

DETD In other embodiments, the epoxidized unsaturated ester used to produce the hydroxy \*\*\*thiol\*\*\* ester is produced from synthetic (or semi-synthetic) unsaturated ester oils. Because the synthetic ester oils can have particular compositions regarding the number of ester groups present, the hydroxy \*\*\*thiol\*\*\* ester would have about the same number of ester groups as the synthetic ester oil. Other, independent properties of the unsaturated ester, whether the unsaturated ester includes natural source or synthetic oils, can be used to further describe the hydroxy \*\*\*thiol\*\*\* ester composition.

DETD The hydroxy \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an epoxidized unsaturated ester composition and can be further limited by the process as described herein. The hydroxy \*\*\*thiol\*\*\* containing natural source oil can also be described using an average molecular weight or an average molecular weight of the side chains.

DETD Cross-Linked \*\*\*Thiol\*\*\* Ester Compositions

DETD In an aspect, the present invention relates to a cross-linked \*\*\*thiol\*\*\* ester composition. Generally, the cross-linked \*\*\*thiol\*\*\* ester molecules are oligomers of \*\*\*thiol\*\*\* esters that are connected together by polysulfide linkages --S.sub.x-- wherein x is an integer greater 1. As the cross-linked \*\*\*thiol\*\*\* ester is described as an oligomer of \*\*\*thiol\*\*\* esters, the \*\*\*thiol\*\*\* esters can be described as the monomer from which the cross-

linked  
 \*\*\*thiol\*\*\* esters are produced.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is an integer greater than 1. In an aspect, the polysulfide linkage may be the polysulfide linkage --S.sub.Q--, wherein Q is 2, 3, 4, or mixtures thereof. In other embodiments, Q can be 2; alternatively, 3; or alternatively, 4.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having at least 3 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, 5 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, 7 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; or alternatively, 10 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages. In yet other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having from 3 to 20 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, from 5 to 15 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; or alternatively, from 7 to 12 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight greater than 2,000. In other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight greater than 5,000; or alternatively, greater than 10,000. In yet other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight ranging from 2,000 to 20,000; alternatively, from 3,000 to 15,000; or alternatively, from 7,500 to 12,500.

DETD In an aspect, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content greater than 0.5. In other embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content greater than 1; alternatively, greater than 2;



alternatively,  
greater than 4. In yet other embodiments, the \*\*\*thiol\*\*\*  
ester monomers and the \*\*\*thiol\*\*\* ester oligomers have a total  
\*\*\*thiol\*\*\* sulfur content from 0.5 to 8; alternatively, from  
4 to 8;  
or alternatively, 0.5 to 4.  
DETD In an aspect, the \*\*\*thiol\*\*\* ester monomers and  
\*\*\*thiol\*\*\*  
ester oligomers have a total sulfur content greater than 8. In  
some  
embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\*  
ester oligomers have a total sulfur content greater than 10;  
alternatively, greater than 12. In yet other embodiments, the  
\*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester  
oligomers have a  
total sulfur content ranging from 8 to 15 weight percent;  
alternatively,  
from 9 to 14; or alternatively, from 10 to 13.  
DETD The cross-linked \*\*\*thiol\*\*\* ester compositions can also be  
described as a product produced by the process comprising  
contacting a  
\*\*\*thiol\*\*\* ester with oxidizing agent and can be further  
limited by  
the process as described herein.  
DETD The present invention advantageously includes sulfide-containing  
ester  
compositions as embodiments of the present invention. Generally,  
the  
sulfide-containing ester compositions can be described as  
containing  
molecules having at least one ester group and a least one sulfide  
group  
within each molecule. The sulfide-containing esters used in the  
present  
invention can be produced by contacting either an unsaturated  
ester or  
an epoxidized unsaturated ester with a \*\*\*thiol\*\*\* containing  
compound as described herein.  
DETD The feedstock unsaturated esters can contain multiple carbon-  
carbon  
double bonds per unsaturated ester molecule. The carbon-carbon  
double  
bond reactivity and statistical probability, however, dictate  
that each  
sulfide-containing ester molecule of the \*\*\*thiol\*\*\* -  
containing  
ester composition produced from the unsaturated ester composition  
will  
not have the same number of sulfide groups, number of unreacted  
carbon-carbon double bonds, molar ratio of carbon-carbon double  
bonds to  
sulfide groups, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\*  
groups  
and other herein disclosed quantities of functional groups and  
molar  
ratios. Additionally, the feedstock unsaturated esters can also  
comprise  
a mixture of individual unsaturated esters having a different  
number of

carbon-carbon double bonds and/or ester groups. Many of these properties are discussed herein as an average number of the groups per sulfide-containing ester molecule within the sulfide-containing ester composition or average ratio per \*\*\*thiol\*\*\* -containing ester molecule within the sulfide-containing ester composition.

DETD In embodiments related to the sulfide-containing ester that is produced from an epoxidized unsaturated ester, the feedstock epoxidized unsaturated esters can contain multiple \*\*\*epoxide\*\*\* groups per unsaturated ester molecule. Individual \*\*\*epoxide\*\*\* group reactivity and statistical probability dictate that each sulfide-containing ester molecule of the sulfide-containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted \*\*\*epoxide\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to sulfide groups, and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock epoxidized unsaturated esters can also comprise a mixture of individual epoxidized unsaturated ester molecules having a different number of \*\*\*epoxide\*\*\* groups and/or ester groups. Thus, many of these properties are described as an average number of the groups per sulfide-containing ester molecules within the sulfide-containing ester composition or average ratio per \*\*\*thiol\*\*\* -containing ester molecule within the sulfide-containing ester composition.

DETD Minimally, in some embodiments, the sulfide-containing esters comprise at least one ester group per sulfide-containing ester molecule. In some embodiments, the sulfide-containing ester has an average of at least 1.5 ester groups per sulfide-containing ester molecule. Alternatively, the sulfide-containing ester molecules have an average of at least 2 ester groups per sulfide-containing ester molecule; alternatively, an average of at least 2.5 ester groups per sulfide-containing ester molecule; or alternatively, an average of at least 3 ester groups per sulfide-containing ester molecule. In other embodiments, the sulfide-containing esters have an average of from 1.5 to 9 ester groups per sulfide-containing ester molecule; alternatively, an average of from 1.5 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 7 ester groups per sulfide-containing ester molecule; alternatively,

an average of from 2.5 to 5 ester groups per sulfide-containing ester molecule; alternatively, an average of from 3 to 5 ester groups per sulfide-containing ester molecule; or alternatively, an average of from 3 to 4 ester groups per sulfide-containing ester molecule. In yet other embodiments, the hydroxy \*\*\*thiol\*\*\* -containing ester comprises an average of about 3 ester groups per sulfide-containing ester molecule; or alternatively, an average of about 4 ester groups per sulfide-containing ester molecule.

DETD In some embodiments, R.sup.3 comprises at least one functional group. In one aspect, the functional group is selected from the group consisting of a hydroxy group, a carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, and a second \*\*\*thiol\*\*\* group. In some aspects, R.sup.3 comprises at least two functional groups. In some aspects, the functional groups are selected from the group consisting of a hydroxy group, carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, a second \*\*\*thiol\*\*\* group, and mixtures thereof.

DETD The sulfide-containing ester compositions can also be described as a product produced by the process comprising contacting an unsaturated ester with a \*\*\*mercaptan\*\*\* and can be further limited by the process as described herein. In other embodiments, the sulfide-containing ester composition can also be described as a product produced by a process comprising contacting an epoxidized unsaturated ester with a \*\*\*mercaptan\*\*\* and can be further limited by the process as described herein.

DETD Generally, the thioacrylate ester composition can be described as comprising thioacrylate molecules having at least one ester group in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule and at least one thioacrylate group. The ester group(s) that are in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule are hereinafter referred to as "supplementary ester group(s)." The thioacrylate ester composition described herein can be produced by contacting an acrylate composition with a \*\*\*thiol\*\*\* -containing ester composition and/or a

hydroxy        \*\*\*thiol\*\*\* -containing ester composition, both of which are described herein.

DETD        The feedstock        \*\*\*thiol\*\*\*        ester compositions and/or hydroxy  
             \*\*\*thiol\*\*\*        ester compositions can comprise a mixture of molecules that have an average quantity of ester groups,        \*\*\*thiol\*\*\* groups, hydroxy groups, and other groups and molar ratios described herein.

             Additionally, individual        \*\*\*thiol\*\*\*        and hydroxy group reactivity within the        \*\*\*thiol\*\*\*        -containing ester compositions and/or hydroxy        \*\*\*thiol\*\*\*        ester compositions and statistical probability dictate that each thioacrylate ester molecule of the thioacrylate ester composition produced may not have the same number of ester groups, thioacrylate groups, acrylate groups, and other herein disclosed quantities of functional groups, moieties, and molar ratios.

Thus, many of the properties of the thioacrylate ester molecules within the thioacrylate ester composition are described as using an average number of the groups per thioacrylate ester molecule within the thioacrylate ester composition or as an average ratio per thioacrylate ester molecule within the thioacrylate ester composition.

DETD        The thioacrylate ester can also be described as a product produced by the process that includes contacting a        \*\*\*thiol\*\*\*        -containing ester composition with an acrylate composition and can be further limited by the process described herein. In other embodiments, the thioacrylate ester composition can also be described as a product produced by a process that includes contacting a hydroxy        \*\*\*thiol\*\*\*        -containing ester composition with an acrylate composition and can be further limited by the process described herein.

DETD        The present invention advantageously provides a sulfonic acid-containing ester as an embodiment of the present invention. Generally, the sulfonic acid-containing ester of the present invention includes sulfonic acid-containing ester molecules having at least one ester group and a least one sulfonic acid group. The sulfonic acid-containing ester described herein can be produced by contacting a        \*\*\*thiol\*\*\*        ester with an oxidizing agent as described herein. Because the feedstock for the production of the sulfonic acid-containing ester can include multiple        \*\*\*thiols\*\*\*        groups,        \*\*\*thiol\*\*\* group

reactivity and statistical probability dictate that each sulfonic acid-containing ester molecule of the sulfonic acid-containing ester will not have the same number of sulfonic acid groups. Additionally, the feedstock \*\*\*thiol\*\*\* ester can also include a mixture of individual \*\*\*thiol\*\*\* ester molecules having different numbers of groups and/or ester groups. Thus, many of the groups present in the sulfonic acid-containing ester are described herein as an average number of the groups per sulfonic acid-containing ester molecule or an average ratio per sulfonic acid-containing ester molecule within the sulfonic acid-containing ester.

DETD In some embodiments of the present invention, the sulfonic acid ester is substantially free of \*\*\*thiol\*\*\* groups.

DETD The sulfonic acid-containing ester can also be described as a product produced by the process comprising contacting a \*\*\*thiol\*\*\* ester with an oxidizing agent described herein.

DETD Process for Making a \*\*\*Thiol\*\*\* Ester Composition

DETD The present invention advantageously provides processes for producing a \*\*\*thiol\*\*\* ester composition as embodiments of the present invention.

As an embodiment, the present invention advantageously includes a process to produce a \*\*\*thiol\*\*\* ester composition by contacting hydrogen sulfide and an unsaturated ester composition containing unsaturated esters and reacting the hydrogen sulfide and unsaturated esters to form or produce the \*\*\*thiol\*\*\* ester composition.

As another embodiment of the present invention, a process to produce the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, the process includes contacting a composition comprising a polyol with a composition comprising a \*\*\*thiol\*\*\* containing carboxylic acid composition and reacting the polyol and \*\*\*thiol\*\*\* containing carboxylic acid composition to form the \*\*\*thiol\*\*\* ester composition.

DETD In some embodiments of the present invention that include producing \*\*\*thiol\*\*\* ester compositions, the unsaturated ester composition is a natural source oil. In an aspect, the unsaturated ester composition is soybean oil or alternatively castor oil. Other suitable types of unsaturated ester compositions are described herein and can be used in

the processes for producing the \*\*\*thiol\*\*\* ester compositions.

DETD \*\*\*Thiol\*\*\* Esters from Unsaturated Esters

DETD As an embodiment of the present invention, the \*\*\*thiol\*\*\* esters described herein can be produced by a process comprising contacting hydrogen sulfide and an unsaturated ester composition and reacting hydrogen sulfide and the unsaturated ester composition to form the \*\*\*thiol\*\*\* ester composition. In one embodiment, the unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups and an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. In this embodiment, the \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules having a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

DETD The processes for producing the \*\*\*thiol\*\*\* ester composition can be applied to any of the unsaturated esters described herein and used to produce any of the \*\*\*thiol\*\*\* esters described herein. The process for producing the \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process conditions described herein.

DETD The hydrogen sulfide to molar equivalents of unsaturated ester carbon-carbon double bonds molar ratio utilized in the process to produce the \*\*\*thiol\*\*\* ester composition can be any molar ratio that produces the desired \*\*\*thiol\*\*\* ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation:  $\# \text{EQU1} \#$  In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the feedstock unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen sulfide to the unsaturated ester carbon-carbon double bonds of greater than 2. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio can be

from 2 to 500; alternatively, from 5 to 200; alternatively, from 10 to 100; or alternatively, from 100 to 200.

DETD When a continuous reactor is used, a feed unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired \*\*\*thiol\*\*\* ester. Alternatively, the feed unsaturated ester weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed unsaturated ester weight hourly space velocity is 0.1; alternatively, the feed unsaturated ester weight hourly space velocity is 0.25; or alternatively, the feed unsaturated ester weight hourly space velocity is 2.

DETD The time required for the reaction of the unsaturated ester and hydrogen sulfide can be any time required to form the described \*\*\*thiol\*\*\* ester. Generally, the time required for the reaction of the unsaturated ester and hydrogen sulfide is at least 5 minutes.

In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In embodiments, the process to produce the \*\*\*thiol\*\*\* ester further comprises a step to remove excess or residual hydrogen sulfide after reacting the hydrogen sulfide and the unsaturated ester composition. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 0.05 weight percent sulfur; alternatively, less than 0.025 weight percent hydrogen sulfide; or

alternatively, less than 0.01 weight percent hydrogen sulfide.  
DETD The reaction between the unsaturated ester and hydrogen sulfide  
can be performed at any temperature capable of forming the \*\*\*thiol\*\*\*  
ester. In some embodiments, the unsaturated ester and hydrogen  
sulfide can be reacted at a temperature greater than -20.degree. C. In  
other embodiments, the unsaturated ester and hydrogen sulfide can be  
reacted at a temperature greater than 0.degree. C.; alternatively,  
greater than 20.degree. C.; alternatively, greater than 50.degree. C.;  
alternatively, greater than 80.degree. C.; or alternatively, greater than  
100.degree. C. In yet other embodiments, the unsaturated ester and hydrogen  
sulfide can be reacted at a temperature from -20.degree. C. to  
200.degree. C.; alternatively, from 120.degree. C. to 240.degree. C.;  
alternatively, from 170.degree. C. to 210.degree. C.; alternatively, from  
185.degree. C. to 195.degree. C.; alternatively, from 20.degree. C. to  
200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or  
alternatively, from 80.degree. C. to 140.degree. C.  
DETD \*\*\*Thiol\*\*\* esters having a low cyclic sulfide content can  
be produced using the disclosed process. In an aspect, the process  
for producing the \*\*\*thiol\*\*\* ester forms or produces a  
\*\*\*thiol\*\*\* ester having a molar ratio of cyclic sulfide to \*\*\*thiol\*\*\*  
groups of less than 1.5. Additional cyclic sulfide to \*\*\*thiol\*\*\*  
groups molar ratios are disclosed herein.  
DETD In addition to lower cyclic sulfide content, \*\*\*thiol\*\*\*  
esters having a low carbon-carbon double bond to \*\*\*thiol\*\*\* group  
molar ratio can also be produced using the disclosed process. In an  
aspect, the process described herein produces the \*\*\*thiol\*\*\* ester  
having a carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio of  
less than 1.5. Additional carbon-carbon double bond to \*\*\*thiol\*\*\*  
group molar ratios are disclosed herein.  
DETD In some aspects, the process described herein produces the  
\*\*\*thiol\*\*\* ester molecules having an average of greater than  
5 weight percent \*\*\*thiol\*\*\* sulfur. Additional \*\*\*thiol\*\*\* sulfur  
contents are disclosed herein. In other aspects, the process for  
producing a \*\*\*thiol\*\*\* ester forms a \*\*\*thiol\*\*\* ester  
having greater than 40 percent of the \*\*\*thiol\*\*\* ester total side



chains include sulfur. Other percentages of the \*\*\*thiol\*\*\* ester total side chains that include sulfur are disclosed herein.

DETD In some embodiments, the process for producing a \*\*\*thiol\*\*\* ester composition includes contacting an unsaturated ester and hydrogen sulfide and reacting the unsaturated ester and the hydrogen sulfide to form a \*\*\*thiol\*\*\* ester. The \*\*\*thiol\*\*\* ester comprises \*\*\*thiol\*\*\* ester molecules that have a ratio of cyclic \*\*\*thiol\*\*\* groups of less than 1.5.

DETD \*\*\*Thiol\*\*\* Ester from a Polyol and a \*\*\*Thiol\*\*\* Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to produce the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative to produce the \*\*\*thiol\*\*\* ester composition. This process can be applied to any polyol, \*\*\*thiol\*\*\* containing carboxylic acid, or \*\*\*thiol\*\*\* containing carboxylic acid derivative described herein. The process for producing the \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the \*\*\*thiol\*\*\* ester composition can form any \*\*\*thiol\*\*\* ester described herein.

DETD In some embodiments, the \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

DETD The polyol used to produce the \*\*\*thiol\*\*\* ester by contacting a polyol and a \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent (for example a \*\*\*thiol\*\*\* carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described \*\*\*thiol\*\*\* containing ester.

DETD In one aspect, the polyol used to produce the \*\*\*thiol\*\*\* ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments,

the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the \*\*\*thiol\*\*\* ester can have any number of hydroxy groups needed to produce the \*\*\*thiol\*\*\* ester as described herein. In some embodiments, the polyol

- has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the \*\*\*thiol\*\*\* ester is a mixture of polyols. In an embodiment, the mixture of polyols

- has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the \*\*\*thiol\*\*\* ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less

than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\* ester by contacting a polyol and a \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent can be any \*\*\*thiol\*\*\* carboxylic acid mixture comprising \*\*\*thiol\*\*\* carboxylic acids, \*\*\*thiol\*\*\* carboxylic acid equivalent or mixture comprising \*\*\*thiol\*\*\* carboxylic acid equivalents that can produce the described \*\*\*thiol\*\*\* containing ester. When talking about the characteristics \*\*\*thiol\*\*\* carboxylic acid equivalent or \*\*\*thiol\*\*\* carboxylic acid equivalents, properties such as number of carbon atoms, average number of carbon atom, molecular weight or average molecular weight, number of \*\*\*thiol\*\*\* group, and average number of \*\*\*thiol\*\*\* groups, one will understand the these properties will apply to the portion of the \*\*\*thiol\*\*\* carboxylic acid equivalent which adds to the polyol to form the \*\*\*thiol\*\*\* ester.

DETD In an aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\* ester comprises from 2 to 28 carbon atoms. In an embodiment, the \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24 carbon atoms; alternatively, from 12 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms. In other embodiments, a mixture comprising \*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising \*\*\*thiol\*\*\* carboxylic acid equivalents has an average of 2 to 28 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 4 to 26 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 8 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 12 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; or alternatively, from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the

\*\*\*thiol\*\*\* ester has at least 1 \*\*\*thiol\*\*\* group;  
 alternatively  
 2 \*\*\*thiol\*\*\* groups. In some embodiments, a mixture  
 comprising  
 \*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising  
 \*\*\*thiol\*\*\*  
 carboxylic acid equivalents has an average of from 0.5 to 3  
 \*\*\*thiol\*\*\* groups per carboxylic acid and/or carboxylic acid  
 equivalent; alternatively, an average of from 1 to 2  
 \*\*\*thiol\*\*\*  
 groups per carboxylic acid and/or carboxylic acid equivalent.  
 DETD In another aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or  
 \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the  
 \*\*\*thiol\*\*\* ester has a molecular weight greater than 100;  
 alternatively greater than 180; alternatively greater than 240;  
 or  
 alternatively greater than 260. In other embodiments, the  
 \*\*\*thiol\*\*\*  
 carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent  
 has a  
 molecular weight from 100 to 500; alternatively, from 120 to 420;  
 alternatively, from 180 to 420; alternatively, from 240 to 420; a  
 mixture or alternatively, from 260 to 360. In some embodiments, a  
 mixture comprising \*\*\*thiol\*\*\* carboxylic acid and/or mixture  
 comprising \*\*\*thiol\*\*\* carboxylic acid equivalents has an  
 average  
 molecular weight greater than 100 per carboxylic acid and/or  
 carboxylic  
 acid equivalent; alternatively greater than 180 per carboxylic  
 acid  
 and/or carboxylic acid equivalent; alternatively greater than 240  
 per  
 carboxylic acid and/or carboxylic acid equivalent; or  
 alternatively  
 greater than 260 per carboxylic acid and/or carboxylic acid  
 equivalent.  
 In yet other embodiments, the mixture comprising of \*\*\*thiol\*\*\*  
 carboxylic acid and/or mixture comprising \*\*\*thiol\*\*\*  
 carboxylic  
 acid equivalents has an average molecular weight from 100 to 500  
 per  
 carboxylic acid and/or carboxylic acid equivalent; alternatively,  
 from  
 120 to 420 per carboxylic acid and/or carboxylic acid equivalent;  
 alternatively, from 180 to 420 per carboxylic acid and/or  
 carboxylic  
 acid equivalent; alternatively, from 240 to 420 per carboxylic  
 acid  
 and/or carboxylic acid equivalent; a mixture or alternatively,  
 from 260  
 to 360 per carboxylic acid and/or carboxylic acid equivalent.  
 DETD In some aspects, the reaction between the polyol and the  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid and/or \*\*\*thiol\*\*\* containing  
 carboxylic  
 acid derivative occurs in the presence of a solvent. In other  
 aspects  
 the reaction between the polyol and the \*\*\*thiol\*\*\*  
 containing  
 carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid

derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, can include from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof. DETD When a solvent is used for the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester oil; alternatively, less than 15 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 10 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative, or alternatively, from 5

times to 10 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. DETD The equivalent of \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the \*\*\*thiol\*\*\* ester composition can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired \*\*\*thiol\*\*\* ester composition. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio can range from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid.

Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a

temperature greater than 20.degree. C. In other embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree. C.

DETD The time required for the reaction of the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be any time required to form the described \*\*\*thiol\*\*\* ester oil. Generally, the reaction time of the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD When a continuous reactor is used, a feed polyol weight unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired \*\*\*thiol\*\*\* ester. Alternatively, the feed polyol weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed polyol ester weight hourly space velocity is 0.1; alternatively, the feed polyol weight hourly space velocity is 0.25; or alternatively, the feed polyol weight hourly space velocity is 2.

DETD The reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative in a liquid state.

In some embodiments, the reaction between the polyol and the  
\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\*  
containing carboxylic acid derivative is performed at a pressure  
ranging from 0 psia to 2000 psia. In other embodiments, the reaction  
pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and  
500 psia; or alternatively, 0 psia to 300 psia.  
DET D In some embodiments, the process to produce the \*\*\*thiol\*\*\*  
ester by reacting a polyol and the \*\*\*thiol\*\*\* containing  
carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can  
further include a step to remove excess or residual polyol, \*\*\*thiol\*\*\*  
containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing  
carboxylic acid derivative once the polyol has reacted with the  
\*\*\*thiol\*\*\* containing carboxylic acid or \*\*\*thiol\*\*\* containing  
carboxylic acid derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is  
vacuum stripped. In some embodiments, the \*\*\*thiol\*\*\* ester is  
vacuum stripped at a temperature ranging between 25.degree. C. and  
250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In  
other embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert  
gas to remove excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid,  
and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some  
embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert  
gas at a temperature between 25.degree. C. and 250.degree. C.; or  
alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the  
inert gas is nitrogen. Generally, the stripped or sparged \*\*\*thiol\*\*\*  
ester comprises less than 5 excess polyol, \*\*\*thiol\*\*\* containing  
carboxylic acid, or \*\*\*thiol\*\*\* containing carboxylic acid  
derivative. In other embodiments, the stripped or sparged  
\*\*\*thiol\*\*\* ester comprises less than 2 weight percent excess polyol,  
\*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing  
carboxylic acid derivative; alternatively, less than 1 weight percent excess  
polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or  
\*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less  
than 0.5 weight percent excess polyol, \*\*\*thiol\*\*\* containing  
carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid  
derivative.



DETD Process for Making Hydroxy \*\*\*Thiol\*\*\* Ester Composition  
 DETD The present invention advantageously provides processes for producing a hydroxy \*\*\*thiol\*\*\* ester as embodiments of the present invention.  
 As an embodiment, the present invention includes a process to produce the hydroxy \*\*\*thiol\*\*\* ester. The process comprises the steps of contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to form the hydroxy \*\*\*thiol\*\*\* ester. As another embodiment of the present invention, another process to produce the hydroxy \*\*\*thiol\*\*\* ester is provided. In this embodiment, the process comprises the steps of contacting a composition comprising a polyol with a composition comprising an hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or an hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative to form the hydroxy \*\*\*thiol\*\*\* ester.  
 DETD Hydroxy \*\*\*Thiol\*\*\* Ester from Hydrogen Sulfide and an Epoxidized Unsaturated Ester Composition  
 DETD As an embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition is produced by a process comprising the steps of contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to produce the hydroxy \*\*\*thiol\*\*\* ester composition.  
 DETD In some embodiments, the epoxidized unsaturated ester composition includes epoxidized unsaturated esters that have an average of at least 1 ester groups and an average of at least 1 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule.  
 DETD The process for producing or preparing the hydroxy \*\*\*thiol\*\*\* ester composition can be applied to any of the epoxidized unsaturated esters described herein and used to produce any hydroxy \*\*\*thiol\*\*\* ester described herein. The process for producing the hydroxy \*\*\*thiol\*\*\* ester can also include any additional process steps or process conditions as described herein. Additionally, the process for producing the hydroxy \*\*\*thiol\*\*\* ester can form any hydroxy \*\*\*thiol\*\*\* ester described herein.  
 DETD In some aspects, the hydroxy \*\*\*thiol\*\*\* ester is produced

by contacting hydrogen sulfide with the epoxidized natural source oil under the reaction conditions to form the hydroxy \*\*\*thiol\*\*\* ester in the presence of an optional catalyst. In some embodiments, the catalyst can be a heterogeneous catalyst or a homogeneous catalyst. Examples of suitable catalysts are described herein. Additional types of catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The hydrogen sulfide to molar equivalents of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester (hereinafter "hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio") utilized in the process to produce the hydroxy \*\*\*thiol\*\*\* ester can be any hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio that produces the desired hydroxy \*\*\*thiol\*\*\* ester. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation: #EQU2#

In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES \*\*\*Epoxide\*\*\* is the average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio ranges from 0.2 to 5; alternatively, from 0.5 to 4; or alternatively, from 0.75 to 3. In some embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio can be from 0.2 to 500; alternatively, from 0.5 to 400; alternatively, from 1 to 300; alternatively, from 2 to 250; alternatively, 5 to 200; or alternatively,

from 10 to 100.

DETD The time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide can be any time required to form the described hydroxy \*\*\*thiol\*\*\* ester. Generally, the time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide is at least 15 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of greater than 2.5 weight percent \*\*\*thiol\*\*\* sulfur. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. Alternatively, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

DETD In other aspects, the process producing the hydroxy \*\*\*thiol\*\*\* ester composition includes producing hydroxy \*\*\*thiol\*\*\* ester molecules having an average of greater than 40 percent of the sulfide-containing ester total side chains comprise a sulfide group. Additional embodiments wherein the hydroxy \*\*\*thiol\*\*\* ester comprises a percentage of sulfide-containing ester total side chains are described herein.

DETD In embodiments, the process to produce the hydroxy \*\*\*thiol\*\*\* ester further comprises a step to remove residual hydrogen sulfide after reacting the hydrogen sulfide and the epoxidized unsaturated ester composition. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C.

C. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the

inert gas  
is nitrogen. Generally, the stripped or sparged hydroxy  
\*\*\*thiol\*\*\*  
ester comprises less than 0.1 weight percent hydrogen sulfide. In  
other  
embodiments, the stripped or sparged hydroxy \*\*\*thiol\*\*\*  
ester  
comprises less than 0.05 weight percent hydrogen sulfide;  
alternatively,  
less than 0.025 weight percent hydrogen sulfide; or  
alternatively, less  
than 0.01 weight percent hydrogen sulfide.  
DETD The reaction between the hydrogen sulfide and the epoxidized  
unsaturated ester can be performed at any temperature capable of  
forming  
the hydroxy \*\*\*thiol\*\*\* ester. In some embodiments, the  
epoxidized  
unsaturated ester and hydrogen sulfide can be reacted at a  
reaction  
temperature greater than -20.degree. C. In other embodiments, the  
reaction temperature is greater than 0.degree. C.; alternatively,  
greater than 20.degree. C.; alternatively, greater than  
50.degree. C.;  
or alternatively, greater than 80.degree. C. In yet other  
embodiments,  
the reaction temperature ranges from -20.degree. C. to  
200.degree. C.;  
alternatively, from 20.degree. C. to 170.degree. C.; or  
alternatively,  
from 80.degree. C. to 140.degree. C.  
DETD In another aspect, the process to produce a hydroxy  
\*\*\*thiol\*\*\*  
ester produces a hydroxy \*\*\*thiol\*\*\* ester having an  
\*\*\*epoxide\*\*\*  
group to \*\*\*thiol\*\*\* group molar ratio less than 3.3. In  
another  
aspect, the process to produce a hydroxy \*\*\*thiol\*\*\* ester  
produces  
a hydroxy \*\*\*thiol\*\*\* ester having an \*\*\*epoxide\*\*\* group  
to  
\*\*\*thiol\*\*\* group molar ratio less than 2. Other hydroxy  
\*\*\*thiol\*\*\*  
ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar  
ratios are  
described herein. Alternatively, the hydroxy \*\*\*thiol\*\*\*  
ester  
\*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio can  
be less  
than 1.5; alternatively, less than 1.0; alternatively, less than  
0.5;  
alternatively, less than 0.25; or alternatively, less than 0.1.  
In other  
embodiments, the hydroxy \*\*\*thiol\*\*\* ester can be  
substantially free  
of \*\*\*epoxide\*\*\* groups.  
DETD In another aspect, the process to produce hydroxy \*\*\*thiol\*\*\*  
ester  
produces a hydroxy \*\*\*thiol\*\*\* ester wherein at least 20  
percent of  
the side chains comprise an .alpha.-hydroxy \*\*\*thiol\*\*\*

group. Other hydroxy \*\*\*thiol\*\*\* ester embodiments wherein the hydroxy \*\*\*thiol\*\*\* ester contains a percentage of side chains comprising .alpha.-hydroxy \*\*\*thiol\*\*\* groups are described herein.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester from a Polyol and a Hydroxy \*\*\*Thiol\*\*\*

Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to prepare the hydroxy \*\*\*thiol\*\*\* ester is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid to form a hydroxy \*\*\*thiol\*\*\* ester composition. This process can be applied to any polyol, any hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, or any \*\*\*thiol\*\*\* containing carboxylic acid derivative described herein. The process for producing the hydroxy \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process conditions described herein.

Additionally, the process for producing the hydroxy \*\*\*thiol\*\*\* ester composition can form any \*\*\*thiol\*\*\* ester described herein.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD The polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester by contacting a polyol and a hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent (for example a hydroxy \*\*\*thiol\*\*\* carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described \*\*\*thiol\*\*\* containing ester.

DETD In one aspect, the polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10

carbon atoms; alternatively, an average of 2 to 7 carbon atoms;  
alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the hydroxy  
\*\*\*thiol\*\*\* ester can have any number of hydroxy groups needed to produce the  
hydroxy \*\*\*thiol\*\*\* ester as described herein. In some  
embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups;  
alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups;  
or alternatively, 6 hydroxy groups. In other embodiments, the polyol  
comprises at least 2 hydroxy groups; alternatively at least 3  
hydroxy groups; alternatively, at least 4 hydroxy groups; or  
alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other  
embodiments, the polyol comprises from 2 to 8 hydroxy groups;  
alternatively, from 2 to 4 hydroxy groups; or alternatively from  
4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the hydroxy  
\*\*\*thiol\*\*\* ester is a mixture of polyols. In an embodiment,  
the mixture of polyols has an average of at least 1.5 hydroxy groups  
per polyol molecule. In other embodiments, the mixture of polyols has  
an average of at least 2 hydroxy groups per polyol molecule;  
alternatively, an average of at least 2.5 hydroxy groups per polyol molecule;  
alternatively, an average of at least 3.0 hydroxy groups per  
polyol molecule; or alternatively, an average of at least 4 hydroxy  
groups per polyol molecule. In yet another embodiment, the mixture of  
polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule;  
alternatively, an average of 2 to 6 hydroxy groups per polyol  
molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol  
molecule; alternatively, an average of 3 to 4 hydroxy groups per  
polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups  
per polyol molecule; or alternatively, an average of 2.5 to 4.5  
hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to  
produce the hydroxy \*\*\*thiol\*\*\* ester has a molecular weight or  
average molecular weight less than 500. In other embodiments, the polyol  
or mixture of polyols have a molecular weight or average molecular  
weight less than 300; alternatively less than 200; alternatively, less  
than 150; or alternatively, less than 100.

DETD The hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy  
\*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the  
hydroxy \*\*\*thiol\*\*\* ester by contacting a polyol and a hydroxy  
\*\*\*thiol\*\*\*  
carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid  
equivalent can be any hydroxy \*\*\*thiol\*\*\* carboxylic acid  
mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids, hydroxy  
\*\*\*thiol\*\*\* carboxylic acid equivalent or mixture comprising  
hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents that can produce the  
described hydroxy \*\*\*thiol\*\*\* containing ester. When talking about the  
characteristics hydroxy \*\*\*thiol\*\*\* carboxylic acid  
equivalent or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents, properties  
such as number of carbon atoms, average number of carbon atom, molecular  
weight or average molecular weight, number of \*\*\*thiol\*\*\* group, and  
average number of \*\*\*thiol\*\*\* groups, one will understand the  
these properties will apply to the portion of the \*\*\*thiol\*\*\*  
carboxylic acid equivalent which adds to the polyol to form the  
\*\*\*thiol\*\*\* ester.

DETD In an aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or  
hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to  
produce the \*\*\*thiol\*\*\* ester comprises from 2 to 28 carbon atoms. In an  
embodiment, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or  
hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents comprises from 4 to  
26 carbon atoms; alternatively, from 8 to 24 carbon atoms; alternatively,  
from 12 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms.

In other embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\*  
carboxylic acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\*  
carboxylic acid equivalents has an average of 2 to 28 carbon  
atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively,  
from 4 to 26 carbon per carboxylic acid and/or carboxylic acid  
equivalent; alternatively, from 8 to 24 carbon atoms per carboxylic acid  
and/or carboxylic acid equivalent; alternatively, from 12 to 24 carbon  
atoms per carboxylic acid and/or carboxylic acid equivalent; or  
alternatively, from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic  
acid equivalent.

DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid  
and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to

produce the  
alternatively  
2  
comprising  
hydroxy  
comprising  
hydroxy  
average of  
from 0.5 to 3  
carboxylic acid equivalent; alternatively, an average of from 1  
to 2  
equivalent.  
DETD In another aspect, the hydroxy  
and/or  
hydroxy  
produce the  
alternatively, at  
least 2 hydroxy groups. In some embodiments, a mixture comprising  
hydroxy  
comprising  
hydroxy  
average of  
from 0.5 to 3 hydroxy groups per carboxylic acid and/or  
carboxylic acid  
equivalent; alternatively, an average of from 1 to 2 hydroxy  
groups per  
carboxylic acid and/or carboxylic acid equivalent.  
DETD In another aspect, the hydroxy  
and/or  
hydroxy  
produce the  
100;  
hydroxy  
alternatively greater than 180; alternatively greater than 240;  
or  
alternatively greater than 260. In other embodiments, the hydroxy  
carboxylic acid equivalent has a molecular weight from 100 to 500;  
alternatively,  
from 120 to 420; alternatively, from 180 to 420; alternatively,  
from 240  
to 420; a mixture or alternatively, from 260 to 360. In some  
embodiments, a mixture comprising hydroxy  
carboxylic acid  
equivalents has an average molecular weight greater than 100 per  
carboxylic acid and/or carboxylic acid equivalent; alternatively  
greater  
than 180 per carboxylic acid and/or carboxylic acid equivalent;  
alternatively greater than 240 per carboxylic acid and/or  
carboxylic acid  
equivalent; or alternatively greater than 260 per carboxylic  
acid  
and/or carboxylic acid equivalent. In yet other embodiments, the  
mixture



comprising hydroxy    \*\*\*thiol\*\*\*    carboxylic acid and/or mixture  
comprising hydroxy    \*\*\*thiol\*\*\*    carboxylic acid equivalents

has an  
average molecular weight from 100 to 500 per carboxylic acid  
and/or  
carboxylic acid equivalent; alternatively, from 120 to 420 per  
carboxylic acid and/or carboxylic acid equivalent; alternatively,  
from  
180 to 420 per carboxylic acid and/or carboxylic acid equivalent;  
alternatively, from 240 to 420 per carboxylic acid and/or  
carboxylic  
acid equivalent; a mixture or alternatively, from 260 to 360 per  
carboxylic acid and/or carboxylic acid equivalent.

DETD    In some aspects, the reaction between the polyol and the hydroxy  
\*\*\*thiol\*\*\*    containing carboxylic acid and/or hydroxy  
\*\*\*thiol\*\*\*  
containing carboxylic acid derivative occurs in the presence of a  
solvent. In other aspects, the reaction between the polyol and  
the  
hydroxy    \*\*\*thiol\*\*\*    containing carboxylic acid and/or hydroxy  
\*\*\*thiol\*\*\*    containing carboxylic acid derivative occurs in  
the  
substantial absence of a solvent. In aspects wherein the reaction  
between the polyol and the hydroxy    \*\*\*thiol\*\*\*    containing  
carboxylic  
acid and/or hydroxy    \*\*\*thiol\*\*\*    containing carboxylic acid  
derivative occurs in the presence of a solvent, the solvent is  
selected  
from the group consisting of an aliphatic hydrocarbon, an ether,  
an  
aromatic compound, or any combination thereof. Generally, the  
solvent,  
regardless of its chemical class, includes from 1 to 20 carbon  
atoms;  
alternatively, from 3 to 10 carbon atoms. When the solvent  
includes the  
aliphatic hydrocarbon, the aliphatic hydrocarbon is butane,  
isobutane,  
pentane, hexane, heptane, octane, or any mixture thereof. When  
the  
solvent includes the aromatic compound, the aromatic compound is  
benzene, toluene, xylene, ethylbenzene, or any mixture thereof.

When the  
solvent includes the ether, the ether is diethyl ether, dipropyl  
ether,  
tetrahydrofuran, and any mixture thereof.

DETD    When a solvent is used for the reaction between the polyol and  
the  
hydroxy    \*\*\*thiol\*\*\*    containing carboxylic acid and/or hydroxy  
\*\*\*thiol\*\*\*    containing carboxylic acid derivative, the  
quantity of  
solvent can be any amount that facilitates the reaction. In some  
embodiments, the mass of the solvent is less than 30 times the  
mass of  
the hydroxy    \*\*\*thiol\*\*\*    containing carboxylic acid and/or  
hydroxy  
\*\*\*thiol\*\*\*    containing carboxylic acid derivative. In other  
embodiments, the mass of the solvent is less than 20 times the  
mass of  
the hydroxy    \*\*\*thiol\*\*\*    ester; alternatively, less than 15

times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 10 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, from 5 times to 10 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD The equivalents of hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter referred to as "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the hydroxy \*\*\*thiol\*\*\* ester can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired hydroxy \*\*\*thiol\*\*\* ester. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio ranges from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric

acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid. Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any temperature capable of forming the hydroxy \*\*\*thiol\*\*\* ester.

In some embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree.

C. In other embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree..

DETD The time required for the reaction of the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be any time required to form the described hydroxy \*\*\*thiol\*\*\* ester composition.

Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or

alternatively, from 2 hours and 24 hours.

DETD The reaction between the polyol and the hydroxy \*\*\*thiol\*\*\*  
 containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\*  
 containing  
 carboxylic acid derivative can be performed at any reaction  
 pressure  
 that maintains the polyol and the hydroxy \*\*\*thiol\*\*\*  
 containing  
 carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing  
 carboxylic  
 acid derivative in a liquid state. In some embodiments, the  
 reaction  
 pressure ranges from 0 psia to 2000 psia. In other embodiments,  
 the  
 reaction pressure ranges from 0 psia to 1000 psia; alternatively,  
 from 0  
 psia and 500 psia; or alternatively, from 0 psia to 300 psia.

DETD In some embodiments, the process to produce the hydroxy  
 \*\*\*thiol\*\*\*  
 ester composition by reacting a polyol and the hydroxy  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\*  
 containing  
 carboxylic acid derivative can further include a step to remove  
 excess  
 or residual polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic  
 acid,  
 and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid  
 derivative  
 once the polyol has reacted with the hydroxy \*\*\*thiol\*\*\*  
 containing  
 carboxylic acid or hydroxy \*\*\*thiol\*\*\* containing carboxylic  
 acid  
 derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is  
 vacuum  
 stripped. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester  
 is  
 vacuum stripped at a temperature between 25.degree. C. and  
 250.degree.  
 C.; or alternatively, between 50.degree. C. and 200.degree. C. In  
 other  
 embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an  
 inert  
 gas to remove excess polyol, hydroxy \*\*\*thiol\*\*\* containing  
 carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing  
 carboxylic  
 acid derivative. In some embodiments, the hydroxy \*\*\*thiol\*\*\*  
 ester  
 is sparged with an inert gas at a temperature between 25.degree.  
 C. and  
 250.degree. C., or alternatively, between 50.degree. C. and  
 200.degree.  
 C. In some aspects, the inert gas is nitrogen. Generally, the  
 stripped  
 or sparged hydroxy \*\*\*thiol\*\*\* ester oil comprises less than  
 5  
 excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic  
 acid, or  
 hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In  
 other

embodiments, the stripped or sparged hydroxy \*\*\*thiol\*\*\*  
ester oil  
comprises less than 2 weight percent excess polyol, hydroxy  
\*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy  
\*\*\*thiol\*\*\*  
containing carboxylic acid derivative; less than 1 weight percent  
excess  
polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid,  
and/or  
hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or  
alternatively, less than 0.5 weight percent excess polyol,  
hydroxy  
\*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy  
\*\*\*thiol\*\*\*  
containing carboxylic acid derivative.  
DETD A method of making a thioacrylate containing ester composition  
is  
advantageously provided as another embodiment of the present  
invention.  
The process for producing the thioacrylate containing ester  
comprising  
contacting a \*\*\*thiol\*\*\* ester with an acrylate and  
converting at  
least one \*\*\*thiol\*\*\* group to a \*\*\*thiol\*\*\* acrylate  
group. The  
process can be applied to any of the \*\*\*thiol\*\*\* esters  
described  
herein and used to any thioacrylate ester described herein. The  
process  
for producing the thioacrylate ester can also include any  
additional  
process steps or process conditions described herein.  
DETD The acrylate compound can be any acrylate compound capable of  
reacting  
with a \*\*\*thiol\*\*\* group to form the \*\*\*thiol\*\*\* acrylate  
group.  
In some embodiments, the acrylate compound can be an acrylic  
halide. In  
other embodiments, the acrylate compound can be an acrylic acid.  
In yet  
other embodiments, the acrylate compound can be an acrylic  
anhydride.  
DETD In some aspects, the conversion of the \*\*\*thiol\*\*\* group to  
a  
thioacrylate group occurs in the presence of a solvent. In other  
aspects  
the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate  
group  
occurs in the substantial absence of a solvent. In aspects  
wherein the  
conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group  
occurs  
in the presence of a solvent, the solvent may be an aliphatic  
hydrocarbon, an ether, and aromatic compound. Generally, the  
solvent,  
regardless of its chemical class, includes from 1 to 20 carbon  
atoms; or  
alternatively, from 3 to 10 carbon atoms. When the solvent  
includes the  
aliphatic hydrocarbon, the aliphatic hydrocarbon is butane,

isobutane,  
pentane, hexane, heptane, octane, or any mixture thereof. When  
the solvent includes the aromatic compound, the aromatic compound is  
benzene, toluene, xylene, ethylbenzene, or any mixture thereof.  
When the solvent includes the ether, the ether is diethyl ether, dipropyl  
ether, tetrahydrofuran, or any mixture thereof.  
DETD When a solvent is used for the conversion of the \*\*\*thiol\*\*\*  
group to a thioacrylate group, the quantity of solvent can be any  
amount that facilitates the reaction. In some embodiments, the mass of the  
solvent is less than 30 times the mass of the \*\*\*thiol\*\*\* ester. In  
other embodiments, the mass of the solvent is less than 20 times the  
mass of the \*\*\*thiol\*\*\* ester; alternatively, less than 15 times the  
mass of the \*\*\*thiol\*\*\* ester; alternatively, less than 10 times the  
mass of the \*\*\*thiol\*\*\* ester; or alternatively, less than 5 times  
the mass of the \*\*\*thiol\*\*\* ester. In other embodiments, the mass of  
the solvent is from 2 times to 20 times the mass of the \*\*\*thiol\*\*\*  
ester; alternatively, from 3 times to 15 times the mass of the  
\*\*\*thiol\*\*\* ester; alternatively, 4 times to 15 times the  
mass of the \*\*\*thiol\*\*\* ester; or alternatively, from 5 times to 10 times  
the mass of the \*\*\*thiol\*\*\* ester.  
DETD In some aspects the conversion of the \*\*\*thiol\*\*\* group to  
the thioacrylate group occurs in the presence of a catalyst. In some  
embodiments, the catalyst is homogeneous. In some embodiments,  
the catalyst is an organic amine. Examples of suitable organic amines  
include triethylamine, tripropylamine, tributylamine, and  
pyridine. In other embodiments, the catalyst is heterogeneous. Examples of  
suitable catalysts include Amberlyst A-21 and Amberlyst A-26. Other  
suitable catalysts will be apparent to those of skill in the art and are  
to be considered within the scope of the present invention.  
DETD The conversion of the \*\*\*thiol\*\*\* group to a thioacrylate  
group can be performed at any conversion temperature that is capable of  
converting the \*\*\*thiol\*\*\* group to a thioacrylate group. In some  
embodiments, the conversion temperature is greater than -20.degree. C. In  
other embodiments, the conversion temperature is greater than 0.degree.  
C.; alternatively, greater than 20.degree. C.; alternatively, greater

than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the conversion temperature ranges from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 50.degree. C. to 150.degree. C.

DETD The conversion time required for the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group can be any time required to form the described thioacrylate containing ester. Generally, the conversion time is at least 5 minutes. In some embodiments, the conversion time is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In other embodiments, the conversion time ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; or alternatively, from 45 minutes to 3 hours.

DETD The conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group can be performed at any conversion pressure that maintains the \*\*\*thiol\*\*\* ester and the acrylate compound in the liquid state. In some embodiments, the conversion pressure ranges from 0 psia to 2000 psia. In other embodiments, the conversion pressure ranges from 0 psia to 1000 psia; or alternatively, from 0 psia to 500 psia.

DETD Process for Producing Cross-Linked \*\*\*Thiol\*\*\* Ester

DETD As an embodiment of the present invention, a process for producing a cross-linked \*\*\*thiol\*\*\* ester composition is advantageously provided. Minimally, in some embodiments, the process to produce the cross-linked \*\*\*thiol\*\*\* ester composition comprises contacting a \*\*\*thiol\*\*\* ester composition with an oxidizing agent and reacting the \*\*\*thiol\*\*\* ester composition and an oxidizing agent to form the \*\*\*thiol\*\*\* ester oligomer having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having the structure --S.sub.Q-- , wherein Q is an integer greater than 1. The disclosed method may be applied to any \*\*\*thiol\*\*\* ester described herein to produce any cross-linked \*\*\*thiol\*\*\* ester composition as described herein. The process to produce the cross-linked \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process

conditions as described herein.

DETD When elemental sulfur is used as the oxidizing agent, the quantity of elemental sulfur utilized to form the cross-linked \*\*\*thiol\*\*\* ester composition is determined as a function of the \*\*\*thiol\*\*\* sulfur content of the \*\*\*thiol\*\*\* ester composition. In an aspect, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition is at least 0.5. In some embodiments, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition is at least 5; alternatively, at least 10, alternatively, at least 15, or alternatively, at least 20. In other embodiments, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition ranges from 0.5 to 32; alternatively, ranges from 1 to 24; alternatively, ranges from 2 to 16; or alternatively, ranges from 3 to 10.

DETD In an aspect, the reaction of the \*\*\*thiol\*\*\* ester and elemental sulfur occurs in the presence of a catalyst. The catalyst can be any catalyst that catalyzes the formation of the polysulfide linkage between at least two \*\*\*thiol\*\*\* ester monomers. In some embodiments, the catalyst is an amine. In further embodiments, the catalyst is a tertiary amine.

DETD The formation of the cross-linked \*\*\*thiol\*\*\* ester can occur in a batch reactor or a continuous reactor, as described herein. The formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at a temperature greater than 25.degree. C. In other embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at a temperature greater than 50.degree. C.; alternatively, greater than 70.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester occurs at a temperature from 25.degree. C. to 150.degree. C.; alternatively, from 50.degree. C. to 150.degree. C.; alternatively, from 70.degree. C. to 120.degree. C.; or alternatively, from 80.degree. C. to 110.degree. C.



DETD The time required to form the cross-linked \*\*\*thiol\*\*\* ester can be any time required to form the desired cross-linked \*\*\*thiol\*\*\* ester. Generally, the time required to form the cross-linked \*\*\*thiol\*\*\* ester is at least 15 minutes. In some embodiments, the time required to form the cross-linked \*\*\*thiol\*\*\* ester is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the time required to form the cross-linked \*\*\*thiol\*\*\* ester ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD In embodiments, the process to produce the cross-linked \*\*\*thiol\*\*\* ester further comprises a step to remove residual hydrogen sulfide. In some embodiments the cross-linked \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester is vacuum striped at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester oil is sparged with an inert gas to remove residual hydrogen sulfide. In other embodiments, the cross-linked \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, between 75 and 150.degree. C. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked \*\*\*thiol\*\*\* ester with an inert gas. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked \*\*\*thiol\*\*\* ester an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the inert gas is nitrogen.

DETD Generally, the stripped or sparged cross-linked \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* -containing ester oil comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The present invention advantageously provides processes for producing sulfide-containing esters as embodiments of the present

invention.

Generally, the sulfide-containing esters can be prepared by two processes. As an embodiment of the present invention, the first process used to produce a sulfide-containing ester comprises contacting an unsaturated ester and a \*\*\*mercaptan\*\*\* and reacting the ester and \*\*\*mercaptan\*\*\* to form a sulfide-containing ester.

As another embodiment of the present invention, the second process used to produce a sulfide-containing ester comprises contacting an epoxidized unsaturated ester and a \*\*\*mercaptan\*\*\* sulfide and reacting the unsaturated ester and \*\*\*mercaptan\*\*\* to form a sulfide-containing ester. Additional aspects of the two sulfide-containing ester production processes are described below.

DETD The sulfide-containing esters and sulfide-containing ester compositions described herein can be produced by a process comprising contacting a \*\*\*mercaptan\*\*\* and an unsaturated ester and reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester to form a sulfide-containing ester. The process can be applied to any of the unsaturated esters and \*\*\*mercaptans\*\*\* described herein. The process for producing the sulfide-containing ester can also include any additional process steps or process conditions described herein. Additionally, the process for producing the sulfide-containing ester can form any sulfide-containing ester described herein.

DETD In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, an alcohol, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic

compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an alcohol, the alcohol is methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester; alternatively, less than 15 times the mass of the unsaturated ester; alternatively, less than 10 times the mass of the unsaturated ester; or alternatively, less than 5 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the unsaturated ester; alternatively, from 3 times to 15 times the mass of the unsaturated ester; alternatively, from 4 times to 15 times the mass of the unsaturated ester; or alternatively, from 5 times to 10 times the mass of the unsaturated ester.

DETD The molar ratio of \*\*\*mercaptan\*\*\* to molar equivalents of unsaturated ester carbon-carbon double bonds (herein after "\*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio") utilized in the process to produce the sulfide-containing ester can be any \*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio that produces the desired sulfide-containing ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation:  $\frac{\text{UES MW}}{\text{UES C.dbd.C}}$  In this equation, UES MW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the \*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio is greater than 0.25. In other embodiments, the \*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio is greater than 0.5; alternatively, greater than 0.75; alternatively, greater than 1; alternatively, greater than 1.25; or alternatively, greater than 1.5. In other embodiments, the \*\*\*mercaptan\*\*\* to carbon-carbon double bond

molar ratio can range from 0.25 to 2; alternatively, from 0.5 to 1.5, or alternatively, from 0.75 to 1.25.

DETD In some aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester is catalyzed. The reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester can be catalyzed by a heterogeneous catalyst or homogeneous catalyst, as described herein. In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by a free radical initiator or ultraviolet radiation, as described herein.

DETD The free radical initiator can be any free radical initiator capable of forming free radicals under thermal or light photolysis. Generally, the free radical initiator is selected from the general class of compounds having a --N.dbd.N-- group or a --O-- O-- group. Specific classes of free radical initiators include diazo compounds, dialkyl peroxides, hydroperoxides, and peroxy esters. Specific initiators include azobenzene, 2,2'-azobis(2-methylpropionitrile, 4,4'-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobis(2methylpropane), 2,2'-azobis(2-methylpropionamide) dihydrochloride, methylpropionitrile, azodicarboxamide, tert-butyl hydroperoxide, di-tert-butyl peroxide, octylperbenzoate. In some embodiments, the free radical initiated reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is performed at a reaction temperature within  $\pm 50$  degree. C. of the 1 hour half life of the free radical initiator. In other embodiments, the reaction temperature is within  $\pm 25$  degree. C. of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within  $\pm 20$  degree. C. of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within  $\pm 15$  degree. C. of the 1 hour half life of the free radical initiator; or alternatively, the reaction temperature is within  $\pm 10$  degree. C. of the 1 hour half life of the free radical initiator. In embodiments where the free radical initiated reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by light photolysis, the light can be any light capable creating free radicals. In some embodiments, the light is UV radiation. Other sources of light capable of creating free radicals

will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In another aspect, the reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by UV radiation. In these embodiments, the UV radiation may be any UV radiation capable of initiating the reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester. In some embodiments, the UV radiation is generated by a medium pressure mercury lamp.

DETD The reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester can occur in a batch reactor of a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction time for reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester can be any time required to form the sulfide-containing ester. Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In some embodiments, the process to produce the sulfide-containing ester further comprises a step to remove any residual \*\*\*mercaptan\*\*\* that remains after reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester. In some embodiments, the sulfide-containing ester is vacuum stripped to remove the residual \*\*\*mercaptan\*\*\*. In some embodiments, the sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the sulfide-containing ester is sparged with an inert gas to remove the residual \*\*\*mercaptan\*\*\*. In some embodiments, the sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged sulfide-containing ester comprises less than 5 weight percent of the \*\*\*mercaptan\*\*\*. In other embodiments, the stripped or sparged sulfide-containing

ester comprises less than 2 weight percent of the \*\*\*mercaptan\*\*\* ; alternatively, less than 1 weight percent of the \*\*\*mercaptan\*\*\* ; or alternatively, less than 0.5 weight percent of the \*\*\*mercaptan\*\*\* .

DETD The reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester can be performed at any temperature capable of forming the sulfide-containing ester. In some embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester can be reacted at a reaction temperature of greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester can be reacted at a temperature from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 80.degree. C. to 160.degree. C.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester can be performed at any pressure that maintains the \*\*\*mercaptan\*\*\* and the unsaturated ester in a substantially liquid state. In some embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester can be performed at a reaction pressure ranging from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD Using the disclosed process, sulfide-containing ester hazing a low carbon-carbon double bond to sulfide group molar ratio can be produced. In an aspect, the process for producing the sulfide-containing ester forms a sulfide-containing ester having a carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio of less than 1.5. Additional carbon-carbon double bond to sulfide group molar ratios are disclosed herein.

DETD As another embodiment of the present invention, another process for producing a class of sulfide-containing esters, which includes hydroxy sulfide-containing esters, is advantageously provided. In this embodiment, the hydroxy sulfide-containing esters and hydroxy sulfide-containing ester compositions can be produced by a

process comprising the steps of contacting a \*\*\*mercaptan\*\*\* and an epoxidized unsaturated ester and reacting the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester to produce or form the hydroxy sulfide-containing ester. The process can be applied to any \*\*\*mercaptan\*\*\* and/or any epoxidized unsaturated esters described herein. The process for producing the hydroxy sulfide-containing ester can also include any additional process steps or process conditions as described herein. Additionally, the process for producing the hydroxy sulfide-containing ester can form any hydroxy sulfide-containing ester as described herein.

DETD In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the epoxidized unsaturated ester; alternatively, less than 15 times the mass of the epoxidized unsaturated ester; alternatively, less than 10 times the mass of the epoxidized unsaturated ester; or alternatively,

less than 5 times the mass of the epoxidized unsaturated ester.

In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the epoxidized unsaturated ester; alternatively, from 3 times to 15 times the mass of the epoxidized unsaturated ester; alternatively, from 4 times to 15 times the mass of the epoxidized unsaturated ester; or alternatively, from 5 times to 10 times the mass of the epoxidized unsaturated ester.

DETD The reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can occur using any \*\*\*mercaptan\*\*\* to molar equivalents of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester (hereinafter referred to as " \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio") that is capable of producing the herein described .alpha.-hydroxy \*\*\*thiol\*\*\* esters. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation: ##EQU4##

DETD In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES \*\*\*Epoxide\*\*\* is the average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.2. In other embodiments, the \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio ranges from 0.2 to 10; alternatively, from 0.5 to 8; alternatively, from 0.75 to 5; or alternatively, from 1 to 3.

DETD In some aspects, the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester to produce the desired hydroxy \*\*\*thiol\*\*\* ester. In one aspect, the catalyst is selected from the group consisting of homogeneous and heterogeneous catalysts. In other aspects, the catalyst is selected from the group consisting of zeolites, heterogeneous catalysts, homogeneous catalysts, and mixtures thereof. In another



is aspect, the catalyst is an amine. In other aspects, the catalyst selected from the group consisting of cyclic conjugated amines, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and mixtures thereof.

DETD In some aspects, the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester occurs in the presence of a catalyst.

Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester to produce the desired hydroxy \*\*\*thiol\*\*\* ester. In some embodiments the catalyst is an organic base. In some embodiments, the catalyst can be 1,8-diazabicyclo[5.4.0]undec-7-ene. (What other catalysts may be used?)

DETD The reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can occur in a batch reactor or a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The time required for the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be any reaction time required to form the described hydroxy sulfide-containing ester. Generally, the reaction time is at least 15 minutes. In some embodiments, the reaction time ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; or alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the process to produce the hydroxy sulfide-containing ester further comprises a step to remove the residual \*\*\*mercaptan\*\*\* after reacting the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester. In some embodiments the hydroxy sulfide-containing ester is vacuum stripped. In some embodiments, the hydroxy sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas to remove the \*\*\*mercaptan\*\*\*. In some embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C.

and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy sulfide-containing ester comprises less than 5 weight percent of the \*\*\*mercaptan\*\*\*. In other embodiments, the stripped or sparged hydroxy sulfide-containing ester comprises less than 2 weight percent of the \*\*\*mercaptan\*\*\*; alternatively, less than 1 weight percent of the \*\*\*mercaptan\*\*\*; or alternatively, less than 0.5 weight percent of the \*\*\*mercaptan\*\*\*.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be performed at any reaction temperature capable of forming the hydroxy sulfide-containing ester. In some embodiments, the reaction temperature is greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.;

alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.;

or alternatively, from 80.degree. C. to 140.degree. C.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be performed at any reaction pressure that maintains the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester in a substantially liquid state. In some embodiments, the reaction pressure ranges from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD In another aspect, the process to produce a hydroxy sulfide-containing ester produces a hydroxy sulfide-containing ester having an \*\*\*epoxide\*\*\* group to sulfide group molar ratio less than 2.

Other hydroxy sulfide-containing ester \*\*\*epoxide\*\*\* group to sulfide group molar ratios are described herein. (The next passage needs to be incorporated into the hydroxy \*\*\*thiol\*\*\* ester section along with the first sentence of this paragraph.) Alternatively, the hydroxy sulfide-containing ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio can be less than 1.5; alternatively, less than 1.0;

alternatively, less than 0.5, alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy sulfide-containing ester can be substantially free of

\*\*\*epoxide\*\*\*

groups.

DETD As an embodiment of the present invention, processes for producing a

sulfonic acid-containing ester and for producing a sulfonate-containing

ester are advantageously provided. Generally, the process for producing

the sulfonic acid-containing ester comprises the steps of contacting a

\*\*\*thiol\*\*\* ester and an oxidizing agent and oxidizing at least one

\*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester to produce a sulfonic

acid group. The process for producing the sulfonate-containing ester

comprises the steps of contacting a sulfonic acid-containing ester with

a base and forming a sulfonate-containing ester.

DETD In an embodiment, the process to prepare a sulfonic acid-containing

ester comprises the steps of contacting the \*\*\*thiol\*\*\* ester

and the oxidizing agent and oxidizing the \*\*\*thiol\*\*\* ester to

produce the sulfonic acid-containing ester. Generally the oxidizing agent

oxidizes at least one \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester

to a sulfonate group. The process to produce the sulfonic acid-containing ester composition can be applied to any

\*\*\*thiol\*\*\* ester described herein to prepare any sulfonic acid-containing

ester described herein. In some embodiments, the \*\*\*thiol\*\*\* ester

includes a hydroxy group. For example, the \*\*\*thiol\*\*\* ester can be

any hydroxy \*\*\*thiol\*\*\* ester described herein. The oxidizing agent

can be any oxidizing agent described herein.

DETD In some aspects, the oxidation of the \*\*\*thiol\*\*\* ester occurs in

the presence of a solvent. In some aspects, the solvent is water.

DETD The oxidizing agent that is contacted with the \*\*\*thiol\*\*\*

ester can be any oxidizing agent capable of oxidizing a \*\*\*thiol\*\*\*

group to a sulfonic acid group. In some embodiments, the oxidizing

agent is oxygen. In other embodiments, the oxidizing agent is chlorine. In

other embodiments, the oxidizing agent is dimethyl sulfoxide. In yet

other embodiments, the oxidizing agent is a combination of a hydrogen

halide and a catalytic amount of a dialkyl sulfide, such as dimethyl

sulfoxide.

Other suitable oxidizing agents will be apparent to those of skill in

the art and are to be considered within the scope of the present invention.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed at any temperature capable of converting the \*\*\*thiol\*\*\* ester to a sulfonic acid-containing ester. In some embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than -20.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C.

DETD The time required for the oxidation of the \*\*\*thiol\*\*\* ester can be any time required to form the desired sulfonic acid-containing ester. Generally, the time required for the oxidation of the \*\*\*thiol\*\*\* ester is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour.

In some embodiments, the time required for the oxidation of the \*\*\*thiol\*\*\* ester ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; alternatively, from 45 minutes to 3 hours.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed at any pressure that maintains the \*\*\*thiol\*\*\* ester and the oxidation agent in the proper state, which is not always a liquid state, to oxidize the \*\*\*thiol\*\*\* ester to a sulfonic acid-containing ester. For example, when the oxidation agent is chlorine, the chlorine can be in the gaseous state. In some embodiments, the oxidation of the \*\*\*thiol\*\*\* ester can be performed at a pressure ranging from 0 to 2000 psig. In other embodiments, the oxidation of the \*\*\*thiol\*\*\* ester can be performed at a pressure ranging from 0 to 1000 psig; or alternatively, 0 to 500 psig.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed in a batch reactor or a continuous reactor, as described herein. Additionally, the process to produce the sulfonic acid-containing ester can comprise additional process steps as recognized by those skilled in the art.

DETD The formation of the sulfonate-containing ester can be performed at any temperature capable of converting the sulfonic acid group of the sulfonic acid-containing ester to a sulfonate group. In some embodiments, the sulfonate-containing ester is formed at a temperature greater than -20.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively,

greater than 50.degree. C. In yet other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature ranging from 0.degree. C. to 250.degree. C.; alternatively, from 0.degree. C. to 150.degree. C.; or alternatively, from 20.degree. C. to 100.degree. C.

DETD A preferred sulfur-containing vegetable oil is MVO available from Chevron Phillips Chemical Co. under the tradename Polymercaptan 358. Polymercaptan 358 is made by the free radical addition of hydrogen sulfide to the double bonds in soybean oil. Typically, Polymercaptan 358 has a \*\*\*thiol\*\*\* sulfur content of 5 to 10% and equivalent weights of 640 to 320, respectively.

DETD Another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a MHVO such as mercapto-hydroxy soybean oil. As described herein, a preferred mercapto-hydroxy soybean oil is made by the free radical addition of hydrogen sulfide to epoxidized soybean oil. Typically, the mercapto and hydroxy functionalities are equal and the \*\*\*mercaptan\*\*\* content is about 8.3% \*\*\*thiol\*\*\* sulfur. The equivalent weight of this material is 192, which includes both mercapto and hydroxy functionalities.

DETD Yet another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a CMVO such as sulfur cross-linked mercaptanized soybean oil. Sulfur cross-linked mercaptanized soybean oil is made by the addition of elemental sulfur to mercaptanized soybean oil. In this process, a portion of the \*\*\*mercaptan\*\*\* groups are consumed as cross-linking sites for the sulfur. Typical sulfur cross-linked mercaptanized soybean oil products by Chevron Phillips Chemical Co. include Runs #22, 194, 195, 196 and 197 and have a \*\*\*thiol\*\*\* sulfur content ranging from about 8.0% to 1.4% and equivalent weights ranging from about 400 to about 2250, respectively.

DETD For epoxy polymer encapsulated CRF material made from sulfur-containing vegetable oil, it has been found that the use of a tertiary amine catalyst is highly preferred. The amount used is such to be sufficient to give the desired reaction rate for the production of the encapsulated slow release fertilizer product. A non-limiting example of a suitable

amine catalyst is diazobicycloundecacene also known as  
1,8-diazabicyclo[5,4,0]undec-7-ene [CAS# \*\*\*6674-22-2\*\*\* ] or  
"DBU", which is preferably used in the range of about 0.1% to 0.5% by  
weight of the coating. Other suitable catalyst materials will be apparent  
to those of ordinary skill in the art.

DETD The preferred sulfur-containing vegetable oil to be used in  
production of an epoxy polymer coated CRF material is MHVO such as mercapto-  
hydroxy soybean oil. One such material is mercapto-hydroxy soybean oil  
known as MHSO 566-84 produced by Chevron Phillips Chemical Co. This  
preferred material contains 8.33% \*\*\*thiol\*\*\* sulfur, with an  
equivalent weight of 384, based upon the \*\*\*mercaptan\*\*\* functionality.

DETD The unsaturated ester used as a feedstock to produce the  
\*\*\*thiol\*\*\* ester compositions described herein can be described using a  
number of different methods. One method of describing the unsaturated ester  
feedstock is by the number of ester groups and the number of  
carbon-carbon double bonds that comprise each unsaturated ester  
oil molecule. Suitable unsaturated ester used as a feedstock to  
produce the \*\*\*thiol\*\*\* ester compositions described herein minimally  
comprise at least 1 ester group and at least 1 carbon-carbon double bond.

However, beyond this requirement, the number of ester groups and carbon-  
carbon double bonds comprising the unsaturated esters are independent  
elements and can be varied independently of each other. Thus, the  
unsaturated esters can have any combination of the number of ester groups and  
the number of carbon-carbon double bonds described separately herein.

functional Suitable, unsaturated esters can also contain additional  
groups, such as alcohol, aldehyde, ketone, epoxy, ether, aromatic  
groups, and combinations thereof. As an example, the unsaturated esters  
can also comprise hydroxy groups. An example of an unsaturated ester that  
contains hydroxy groups is castor oil. Other suitable unsaturated  
esters will be apparent to those of skill in the art and are to be  
considered within the scope of the present invention.

DETD In yet another aspect, the polyol or mixture of polyols used to  
produce the unsaturated \*\*\*thiol\*\*\* ester has a molecular weight or  
average molecular weight less than 500. In other embodiments, the polyol  
or

mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD In some embodiments, suitable polyols include 1,2-ethanediol, 1,3-propanediol, 1,4- \*\*\*butanediol\*\*\*, 1,5-pentanediol, 1,6-hexanediol, dimethylolpropane, neopentylpropane, 2-propyl-2-ethyl-1,3-propanediol, 1,2-propanediol, 1,3-\*\*\*butanediol\*\*\*, diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, tripropylene glycol, and polypropylene glycol; cyclohexanedimethanol, 1,3-dioxane-5,5-dimethanol; and 1,4-xylylenedimethanol and 1-phenyl-1,2-ethanediol, trimethylolpropane, trimethylolethane, trimethylolbutane, glycerol, 1,2,5-hexanetriol, pentaerythritol, ditrimethylolpropane, diglycerol, ditrimethylolethane, 1,3,5-trihydroxybenzene, 1,4-xylylenedimethanol, and 1-phenyl-1,2-ethanediol, or any combination thereof. In further embodiments, the polyol is glycerol, pentaerythritol, or mixtures thereof. In other embodiments, the polyol is glycerol, or alternatively pentaerythritol.

DETD Specific carboxylic acids used as a component of the carboxylic acid composition used to produce the unsaturated ester oil can have from 3 to 30 carbon atoms per carboxylic acid molecule. In some embodiments the carboxylic acid is linear. In some embodiments the carboxylic acid is branched. In some embodiments the carboxylic acid is a mixture of linear and branched carboxylic acids. In some embodiments the carboxylic acid can also comprise additional functional groups including alcohols, aldehydes, ketones, and \*\*\*epoxides\*\*\*, among others.

DETD Minimally, the epoxidized unsaturated ester comprises at least one \*\*\*epoxide\*\*\* group. In an embodiment the epoxidized unsaturated ester comprises at least 2 \*\*\*epoxide\*\*\* groups; alternatively, at least 3 \*\*\*epoxide\*\*\* groups; or alternatively, at least 4 \*\*\*epoxide\*\*\* groups.

In other embodiments, the epoxidized unsaturated ester comprises from 2 to 9 \*\*\*epoxide\*\*\* groups; alternatively, from 2 to 4 \*\*\*epoxide\*\*\* groups; alternatively, from 3 to 8 \*\*\*epoxide\*\*\* groups; or alternatively, from 4 to 8 \*\*\*epoxide\*\*\* groups.

DETD In some embodiments, the unsaturated ester comprises a mixture of epoxidized unsaturated esters. In this aspect, the number of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester is best

described as an average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the epoxidized unsaturated esters have an average of at least 1.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule;

alternatively, an average of at least 2 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; or alternatively, an average of at least 3 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In other embodiments, the epoxidized unsaturated esters have average of from 1.5 to 9 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule;

alternatively, an average of from 3 to 8 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of from 2 to 4 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; or alternatively, from of 4 to 8 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule.

DETD The \*\*\*thiol\*\*\* composition can include an average of greater than 0 to about 4 \*\*\*epoxide\*\*\* groups per triglyceride. The \*\*\*thiol\*\*\* composition can also include an average of greater than 1.5 to about 9 \*\*\*epoxide\*\*\* groups per triglyceride.

DETD \*\*\*Mercaptans\*\*\*

DETD Within some embodiments, an unsaturated ester or an epoxidized unsaturated ester is contacted with \*\*\*mercaptan\*\*\*. Within these embodiments, the \*\*\*mercaptan\*\*\* can be any \*\*\*mercaptan\*\*\* comprising from 1 to 20 carbon atoms. Generally, the \*\*\*mercaptan\*\*\* can have the following structure: HS--R.sup.3 wherein R3 is a C1 to C20 organyl groups or a C1 to C20 hydrocarbyl groups. In further embodiments the R3 can be a C2 to C10 organyl group or a C2 to C10 hydrocarbyl group. In some embodiments, the \*\*\*mercaptan\*\*\* composition comprises a solvent. In one aspect, the \*\*\*mercaptan\*\*\* composition comprises at least one other functional group.

DETD The at least one other functional group can be selected from several different groups. For example, the at least one other functional group is an alcohol group, a carboxylic alcohol group, a carboxylic ester group, an amine group, a sulfide group, a \*\*\*thiol\*\*\* group, a methyl or ethyl ester of a carboxylic acid group, or combinations thereof. Other types of functional groups will be apparent to those of skill in the art and are to be considered within the scope of the



present invention.

DETD In some embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of 3-mercaptopropyl-trimethoxysilane, 2-mercaptopyridine, 4-mercaptopyridine, 2-mercaptopyrimidine, mercaptopyruvic acid, mercaptosuccinic acid, 2-mercaptonicotinic acid, 6-mercaptonicotinic acid, 2-mercaptophenol, 4-mercaptophenol, 3-mercapto-1,2-propanediol, 3-mercapto-1,2-propanediol, 3-mercapto-1-propanesulfonic acid, 1-mercapto-2-propanol, 3-mercapto-1-propanol, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzyl alcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethanesulfonic acid, 2-mercaptoethanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 16-mercaptohexadecanoic acid, 6-mercapto-1-hexanol, 4'-mercaptoacetanilide, mercaptoacetic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptothiazoline, 3-mercapto-1H-1,2,4-triazole, 11-mercaptoundecanoic acid, 1-mercapto-1-undecanol, or combinations thereof.

DETD In some embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of beta-mercaptoethanol, 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol, mercaptosuccinic acid, and mixtures thereof.

In further embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of beta-mercaptoethanol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol, and mixtures thereof. In further embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, and mixtures thereof. In yet further embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, mercaptosuccinic acid, and mixtures thereof.

DETD Within some embodiments, the inventive compositions described

herein are reacted with an isocyanate compound to produce a polythiourethane composition. The isocyanate may be any isocyanates capable of reacting with the \*\*\*thiol\*\*\* esters, hydroxy \*\*\*thiol\*\*\* esters, and a cross-linked \*\*\*thiol\*\*\* esters described herein to form a polyurethane composition. Generally, the isocyanate compound has at least two isocyanate groups.

DETD In order to quantitatively measure the \*\*\*thiol\*\*\* sulfur, the \*\*\*thiol\*\*\* sulfur analyses were conducted using silver nitrate titration in accordance with ASTM D3227, with the following modifications designed to minimize probe fouling by silver salts: the samples were diluted in a known mass of tetrahydrofuran. The silver nitrate concentration was 0.01 N standardized against potassium iodide.

DETD \*\*\*Thiol\*\*\* sulfur was analyzed by three different tests. The first test used was the modified ASTM D3227, which resulted in a \*\*\*thiol\*\*\* sulfur measurement of 4.64%. The second test used to measure the \*\*\*thiol\*\*\* sulfur was SLP-1204, which is a test developed by Chevron Phillips Chemical Company LLP. By using the SLP-1204 test, the resulting \*\*\*thiol\*\*\* sulfur measurement was 4.28%. Lastly, the total sulfur was measured by combustion analysis, which resulted in a total sulfur measurement of 4.27%.

DETD Vegetable oil (42 kg) was charged to a 100-gallon holding vessel. The vessel was purged with nitrogen and returned to atmospheric pressure. Hydrogen sulfide (174 kg) was charged to the holding vessel. The vessel temperature was controlled from 25-30.degree. C. while the pressure was typically maintained between 380-400 psig. The reactants were continuously rolled from the holding tank through a stainless steel tubular photochemical reactor containing a 7.5 KW Hanovia medium pressure mercury lamp contained within a quartz tube. Reactor temperature, pressure, and composition were monitored over the course of the reaction. The reaction time was dependent upon reaching a desired composition of \*\*\*thiol\*\*\* sulfur. Upon completion, the unreacted hydrogen sulfide was slowly vented from the system. Residual H.sub.2S was removed at 100.degree. C. and reduced pressure while passing nitrogen through a nitrogen sparge tube. The product was drained from the bottom of the reactor into a clean drum. The \*\*\*thiol\*\*\*

sulfur measurements were 11.0% when using the modified ASTM D3227, 8.74% when using SLP-1204, and the total sulfur was 11.21% when using combustion analysis (total sulfur).  
 DETD The resulting mercaptanized soybean oil was subjected to nitrogen sparging under reduced pressure at 100.degree. C. for a period of 4 hours to remove any residual hydrogen sulfide. The \*\*\*thiol\*\*\* sulfur measurements were 13.0% when using the modified ASTM D3227, 9.82% when using SLP-1204, and 11.69% when using combustion analysis.  
 DETD Table 1 provides the properties of the mercaptanized soybean oil produced in examples 1-3.  
 TABLE 1

# Mercaptanized Soybean Oil Product Properties

C.dbd.C	Cyclic Sulfide to ***Thiol*** Sulfur.sup..dagger. Group		
	to ***Thiol*** (wt %)	groups Molar Ratio	***Thiol*** Molar Ratio
Example			
1	4.28	0.02	2.79
2	11.0	0.03	0.26
3	13.0	0.03	0.51

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by the modified ASTM D3227  
 DETD Soybean oil was charged to a 1000 gallon stirred reactor.  
 Hydrogen sulfide was then charged to the reactor. After the hydrogen sulfide was charged to the reactor, the stirrers and the UV lamps were turned on and the reaction allowed to build temperature and pressure as the reaction proceed. The reaction was continued until a minimum \*\*\*thiol\*\*\* sulfur content of 8 weight percent was achieved. After reaction was completion, the excess hydrogen sulfide was flashed from the reactor.  
 For runs 2-5, the mercaptanized soybean oil product underwent an additional hydrogen sulfide stripping step comprising stripping hydrogen sulfide from the product under vacuum, 50 mm Hg, at 250.degree. F. (only true for runs 2-5).  
 DETD Table 3 provides the details of the analysis of the mercaptanized soybean oil producing in the five 1000 gallon reactor runs.  
 TABLE 3

# 1000 gallon reactor Mercaptanized Soybean Oil Product Properties Side Chain

	***Thiol***	Cyclic Sulfide to	***Thiol***	C.dbd.C
to	***Thiol***	Containing		
Run	Sulfur.sup..dagger.	Group	groups	
	***Thiol***	Groups		
Number	(wt %)	Molar Ratio		(%)
1	9.3	--	--	71.6
2	9.6	0.04	0.48	72.3
3	9.2	0.03	0.59	69.1
4	9.3	0.03	0.62	71.6
5	10.1	0.03	0.54	72.3

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by Raman spectroscopy

Mercaptanized Castor Bean Oil

DEID The analytical properties of the two mercaptanized castor oil products

are provide in Table 4.

TABLE 4

Mercaptanized Castor Oil Product Properties

	***Thiol***	C.dbd.C to	Side Chain
Containing	Sulfur.sup..dagger.	***Thiol***	groups
***Thiol***			
Groups			
Example	(wt %)	Molar Ratio	(%)
1	6.4	0.52	64.1
2	7.4	0.26	77.7

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by Raman spectroscopy

Mercaptohydroxy Soybean Oil Synthetic Procedure

DEID Epoxidized Soybean Oil (700 g, .about.0.7 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.7 g, 30.5 mmol) were charged

to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630

psig. Hydrogen sulfide (H.sub.2S, 132.0 g, 3.87 mol) was then pressured

into the stirred reactor contents through a dip tube in the liquid

space. The reaction mixture was heated and maintained at 85.degree. C.

with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 351 psig to 219 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S

was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under

vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a

\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content

of 7.53  
wt. %, 2.5 SH/molecule, or 2.35 meq SH/g. Combustion analysis indicated  
C, 64.37%, H, 10.20%, N, <0.15%, and S, 9.51%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and  
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
charged  
to a 1-L Hastelloy C autoclave reactor, and the vessel was  
pressure  
tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99  
mol) was  
then pressured into the stirred reactor contents through a dip  
tube in  
the liquid space. The reaction mixture was heated and maintained  
at  
97.degree. C. with stirring for 14 hrs, during which time the  
reactor  
pressure decreased from a maximum of 509 psig to 229 psig. The  
stirrer  
was stopped and while still warm (90-95.degree. C.), excess  
H.sub.2S was  
slowly vented to a low-pressure flare. The reactor vapor space  
was then  
swept with N.sub.2 for 1 hr and the reactor contents drained warm  
(80-85.degree. C.). The reaction product was N.sub.2 sparged  
under  
vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
residual  
H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content  
of 4.14  
wt. %, 1.4 SH/molecule, or 1.29 meq SH/g. Combustion analysis  
indicated  
C, 65.18%, H, 10.17%, N, <0.15%, and S, 7.80%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and  
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
charged  
to a 1-L Hastelloy C autoclave reactor, and the vessel was  
pressure  
tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99  
mol) was  
then pressured into the stirred reactor contents through a dip  
tube in  
the liquid space. The reaction mixture was heated and maintained  
at  
85.degree. C. with stirring for 10 hrs, during which time the  
reactor  
pressure decreased from a maximum of 578 psig to 489 psig. The  
stirrer  
was stopped and while still warm (80-85.degree. C.), excess  
H.sub.2S was  
slowly vented to a low-pressure flare. The reactor vapor space  
was then  
swept with N.sub.2 for 1 hr and the reactor contents drained warm  
(80-85.degree. C.). The reaction product was N.sub.2 sparged  
under  
vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
residual  
H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*\*thiol\*\*\* sulfur (titration with modified ASTM D3227)

content of  
8.28 wt. %, 2.8 SH/molecule, or 2.58 meq SH/g. Combustion  
analysis indicated C, 65.24%, H, 9.52%, N, 0.18%, and S, 9.53%.  
DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and  
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
charged to a 1-L Hastelloy C autoclave reactor that was pressure tested  
to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then  
pressured into the stirred reactor contents through a dip tube in the  
liquid space. The reaction mixture was heated and maintained at  
85.degree. C. with stirring for 12 hrs, during which time the reactor pressure  
decreased from a maximum of 587 psig to 498 psig. The stirrer was  
stopped and while still warm (80-85.degree. C.), excess H.sub.2S  
was slowly vented to a low-pressure flare. The reactor vapor space  
was then swept with N.sub.2 for 1 hr and the reactor contents drained warm  
(80-85.degree. C.). The reaction product was N.sub.2 sparged  
under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
residual H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content  
of 8.24 wt. %, 2.8 SH/molecule, or 2.57 meq SH/g. Combustion analysis  
indicated C, 63.39%, H, 10.01%, N, <0.15%, and S, 8.76%.  
DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and  
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
charged to a 1-L Hastelloy C autoclave reactor, and the vessel was  
pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99  
mol) was then pressured into the stirred reactor contents through a dip  
tube in the liquid space. The reaction mixture was heated and maintained  
at 85.degree. C. with stirring for 8 hrs, during which time the  
reactor pressure decreased from a maximum of 606 psig to 537 psig. The  
stirrer was stopped and while still warm (80-85.degree. C.), excess  
H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space  
was then swept with N.sub.2 for 1 hr and the reactor contents drained warm  
(80-85.degree. C.). The reaction product was N.sub.2 sparged  
under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
residual H.sub.2S. The resulting light yellow, viscous sticky oil had a  
\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content  
of 7.34 wt. %, 2.5 SH/molecule, or 2.29 meq SH/g. Combustion analysis

indicated

C, 64.47%, H, 10.18%, N, <0.15%, and S, 8.40%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630

psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured

into the stirred reactor contents through a dip tube in the liquid

space. The reaction mixture was heated and maintained at 85.degree. C.

with stirring for 6 hrs, during which time the reactor pressure decreased from a maximum of 586 psig to 556 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S

was slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content

of 5.93 wt. %, 2.0 SH/molecule, or 1.85 meq SH/g. Combustion analysis indicated

C, 65.26%, H, 10.19%, N, <0.15%, and S, 8.43%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure

tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in

the liquid space. The reaction mixture was heated and maintained at

85.degree. C. with stirring for 4 hrs, during which time the reactor

pressure decreased from a maximum of 595 psig to 554 psig. The stirrer

was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content

of 5.36 wt. %, 1.8 SH/molecule, or 1.67 meq SH/g. Combustion analysis indicated

C, 65.67%, H, 10.17%, N, 0.34%, and S, 9.84%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and  
 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
 charged to a 1-L Hastelloy C autoclave reactor that was pressure tested  
 to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then  
 pressured into the stirred reactor contents through a dip tube in the  
 liquid space. The reaction mixture was heated and maintained at  
 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure  
 decreased from a maximum of 577 psig to 519 psig. The stirrer was  
 stopped and while still warm (80-85.degree. C.), excess H.sub.2S  
 was slowly vented to a low-pressure flare. The reactor vapor space  
 was then swept with N.sub.2 for 1 hr and the reactor contents drained warm  
 (80-85.degree. C.). The reaction product was N.sub.2 sparged  
 under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove  
 residual H.sub.2S. The resulting light yellow, viscous sticky oil had a  
 \*\*\*thiol\*\*\* sulfur (titration with AgNO.sub.3) content of  
 5.85 wt. %, 2.0 SH/molecule, or 1.82 meq SH/g. Combustion analysis indicated  
 C, 65.09%, H, 10.15%, N, 0.35%, and S, 10.63%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and  
 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were  
 charged to a 1-L Hastelloy C autoclave reactor, and the vessel was  
 pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99  
 mol) was then pressured into the stirred reactor contents through a dip  
 tube in the liquid space. The reaction mixture was heated and maintained  
 at 85.degree. C. with stirring for 2 hrs, during which time the  
 reactor pressure decreased from a maximum of 577 psig to 508 psig. The  
 stirrer was stopped and while still warm (80-85.degree. C.), excess  
 H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space  
 was then swept with N.sub.2 for 1 hr and the reactor contents drained warm  
 (80-85.degree. C.). The reaction product was N.sub.2 sparged  
 under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove  
 residual H.sub.2S. The resulting light yellow, viscous sticky oil had a  
 \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content  
 of 5.07 wt. %, 1.7 SH/molecule, or 1.58 meq SH/g. Combustion analysis  
 indicated C, 63.96%, H, 10.01%, N, 0.35%, and S, 11.22%.

DETD Table 5 provides the properties of the mercaptohydroxy soybean  
 oil



samples produced in Examples 1-10.  
TABLE 5

per Example	***Epoxides***		***Mercaptan***		
	Reaction	Reaction	Sulfur	SH per	groups left
	***Epoxide*** Time (hrs) molecule.sup.3	:SH Temp (.degree. C.) Molar Ratio	(wt. %).sup.1	molecule.sup.2	
1	0	N/A	N/A	0	4.3
--					
2	8	85	7.53	2.5	1.8
3	0.72 14	97	4.14	1.4	2.9
4	2.07 10	85	8.28	2.8	1.5
5	0.54 12	85	8.24	2.8	1.5
6	0.54 8	85	7.34	2.5	1.8
7	0.72 6	85	5.93	2.0	2.3
8	1.15 4	85	5.36	1.8	2.5
9	1.40 4	85	5.85	2.0	2.3
10	1.15 2	85	5.07	1.7	2.6
	1.529				

.sup.1Thiol sulfur was determined by silver nitrate oxidation using ASTM D 3227

.sup.2Determined by wt. % \*\*\*thiol\*\*\* sulfur

.sup.3Determined by subtracting the SH/molecule from the starting material

\*\*\*epoxide\*\*\* content

DETD Epoxidized soybean oil and the catalyst were charged to a 1-L Hastelloy

C autoclave reactor, and the vessel was pressure tested to 1000 psig.

Hydrogen sulfide was then pressured into the stirred reactor contents

through a dip tube in the liquid space. The reaction mixture was heated

and maintained at temperature a set period of time with stirring for 12

hrs. During the reaction time the reactor pressure usually decreased. At

the end of the reaction time, the stirrer was stopped and excess H.sub.2S was slowly vented while the reaction mixture was warm to

a low-pressure flare. The reactor vapor space was then swept with

N.sub.2 for 1 hr and the reactor contents drained. The reaction product

was N.sub.2 sparged under vacuum (<50 mmHg) at 100.degree. C. for 16

hrs to  
 remove residual H.sub.2S. Table 6 provides the reaction  
 conditions used  
 to produce the mercaptohydroxy soybean oils for several runs and  
 the  
 \*\*\*thiol\*\*\* sulfur content of the mercaptohydroxy soybean  
 oils  
 produced.  
 TABLE 6

# Mercaptohydroxy Soybean Oil Production Runs

Run	Epoxidized Soybean Oil Temperature (g)	Time (wt. %)	Catalyst (g)	H.sub.2S ***Thiol*** (g)	H.sub.2S: Sulfur.sup.a Molar Ratio	***Epoxide*** (.degree. C.)
556-41.sup..dagger.	249.6			1.950	214.0 5.86	64
728	5.69					
556-53.sup..dagger.	250.0			2.000	213.0 5.81	100
370	9.04					
556-47.sup..dagger.	250.5			1.050	213.0 5.81	101
720	10.47					
407-81D.sup..dagger.	500.0			4.200	255.0 3.49	85
480	7.53					
407-86.sup..dagger.	600.0			5.000	204.0 2.07	85
600	8.28					
556-79.sup..dagger-dbl.	250.0			2.600	214.0 5.83	100
720	6.68					
556-80.sup..dagger-dbl.	251.0			5.000	214.0 5.81	100
720	9.51					

.sup..dagger.Catalyst was DBU  
 .sup..dagger-dbl.catalyst was triethylamine (TEA)  
 .sup.aThiol sulfur measured by silver nitrate titration using modified  
 ASTM D  
 3227  
 DETD Run number 407-86 was subjected to the sodium methoxide  
 methanolysis  
 procedure and subsequently analyzed by GC/MS. The GS/MS analysis  
 indicated that the product had \*\*\*epoxide\*\*\* group to  
 \*\*\*thiol\*\*\*  
 group molar ratio of approximately 0.14. The methanolysis data  
 also  
 indicated that an average of 80.4 percent of the product  
 mercaptohydroxy  
 soybean oil contained sulfur.  
 DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % \*\*\*thiol\*\*\*  
 sulfur,) was charged to a three necked flask along with elemental  
 sulfur  
 pellets (9.6 g). The reaction mixture was heated to 120.degree.  
 C. until  
 sulfur dissolved and then cooled to 99.degree. C. Tributylamine  
 (4.8 g)  
 was charged to the reaction mixture with an addition funnel drop  
 wise.  
 The reaction mixture was mixed at 90.degree. C. for 2 hrs.  
 H.sub.2S

evolution was observed. The reaction product (904.8 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 6.33 wt. % (by modified ASTM D3227). The elemental combustion analysis was 70.19% C, 10.37% H; and 11.21% S.

DETD Mercaptanized soybean oil (900.0 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (36.0 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 36 hrs. H.sub.2S evolution was observed. The reaction product (825.6 g) was sparged with N.sub.2 under vacuum at 90.degree. C. for 36 hrs to remove residual H.sub.2S. The reaction product was then sparged with N.sub.2 under vacuum at 110.degree. C. for 3 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 2.36 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.90% C; 11.07% H; and 12.25% S.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (18.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 101.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (901.5 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 4.9 wt. % (by modified ASTM D3227). The elemental combustion analysis was 69.58% C, 11.25% H; and 11.31% S.

DETD Mercaptanized soybean oil (900.2 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (45.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs.

H.sub.2S evolution was observed. The reaction product (915.0 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a **\*\*\*thiol\*\*\*** sulfur of 1.41 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.35% C, 10.98% H; and 13.28% S. Numerous polythiourethane compositions were prepared by reacting a **\*\*\*thiol\*\*\*** ester composition with a diisocyanate in the presence of a catalyst by using the processes described herein for preparing such polythiourethane compositions. The compositions were produced using the different variables of feedstocks, diisocyanates, stoichiometry, and catalysts shown in Table 8. Once every combination of variable was used, over 1200 compositions were produced. Each of the feedstocks were reacted with each of the diisocyanates at each of the stoichiometries with each of the catalysts listed to produce the 1200+ compositions. The stoichiometry was based upon a **\*\*\*thiol\*\*\*** ester composition (MSO, MHSO, CMSO, MCO) active hydrogen ( **\*\*\*thiol\*\*\*** and hydroxyl group) to diisocyanate equivalent ratio. For example, castor oil was reacted with toluene diisocyanate at a stoichiometric value of 1.25 while using Jeffol.RTM. A-480 as the catalyst. As another example, a **\*\*\*thiol\*\*\*** ester composition was reacted with methane diisocyanate at a stoichiometric value of 0.9 while using the DABCO catalyst. DETD In the first MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate at a **\*\*\*thiol\*\*\*** to isocyanate mole ratio of 0.95. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer. DETD In the second MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate M20S at a

\*\*\*thiol\*\*\* to isocyanate mole ratio of 1.00. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the polythiourethane compositions, the feedstock \*\*\*thiol\*\*\* ester compositions that were used included MSO (mercaptanized soybean oil), MHSO (mercaptohydroxy soybean oil), CMSO (cross-linked mercaptanized soybean oil), castor oil, and MCO (mercaptanized castor oil). The diisocyanates that were used to produce these compositions included MDI (4,4'-methylenebis(phenyl) diisocyanate), HMDI (4,4'-methylenebis(cyclohexyl) diisocyanate, which is also known as hydrogenated MDI), TDI (tolylene 2,4-diisocyanate), HDI (1,6-diisocyanatohexane, which is also known as hexamethylene diisocyanate), and Luprinate.TM. M20S (which is an oligomerized form of MDI and is also referred to as polymeric MDI that is produced by BASF Corporation). The catalysts that were used included DABCO (diazabicyclooctane--di-tertiary amine), DBTDL (dibutyl tin dilaurate--organometallic catalyst), Jeffol.RTM. A-480 (which is a tertiary amine polyol produced by Huntsman Based Chemicals), and BDMA (benzyltrimethylamine).

DETD In the Fertilizer Examples, the following materials were used:

A: Fertilizer particles--granular fertilizer grade urea, SGN 250, commercially available from Agrium;

B1: Mercaptanized soybean oil (an example of MVO discussed above)--Polymercaptan 358, available from Chevron Phillips Chemical Co.;

8.65% \*\*\*thiol\*\*\* sulfur; 370 equivalent weight; viscosity of 510.6 cSt @ 21.degree. C.;

B2: Mercapto-hydroxy soybean oil (an examples of MHVO discussed above)--A mercapto-hydroxy soybean oil made by the free radical addition of hydrogen sulfide to epoxidized soybean oil; the mercapto and hydroxy functionalities are equal; 8.335% \*\*\*thiol\*\*\* sulfur; equivalent weight 192 (including both mercapto and hydroxy functionalities);

B3: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil

made by the addition of elemental sulfur to mercaptanized soybean oil;  
 \*\*\*thiol\*\*\* sulfur content 6.33%; equivalent weight 506;  
 B4: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO  
 discussed above)--A sulfur cross-linked mercaptanized soybean oil  
 made by the addition of elemental sulfur to mercaptanized soybean oil;  
 \*\*\*thiol\*\*\* sulfur content 7.64%; equivalent weight 419;  
 cross-linkcross-link  
 C1: Isocyanate #17--A polymeric MDI, commercially available from BASF  
 Canada,  
 equivalent weight of 133;  
 C2: Epoxy resin--5 minute epoxy resin, commercially available from ITW  
 Devcon,  
 Danvers, Mass. 01923 USA, equivalent weight 198;  
 D1: Organic additive--Gulftene C30-HA alpha olefin wax, commercially  
 available  
 from Chevron Phillips Chemical Co., melting point 65.degree.  
 C.-80.degree. C.;  
 D2: Organic additive--Calwax 170, a microcrystalline wax commercially  
 available from Calwax Corporation;  
 E: Cross-linking agent--Jeffol A480, commercially available from  
 Huntsman  
 Polyurethanes; equivalent weight of 120; functionality 4.0;  
 viscosity of  
 4000 cPs @25C;  
 F1: Amine catalyst: Exp-9, commercially available from Huntsman  
 Polyurethanes;  
 and  
 F2: Amine catalyst: 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), CAS#  
 \*\*\*6674-2-2\*\*\*  
 DETD Analysis of the \*\*\*Thiol\*\*\* Containing Esters, Hydroxy  
 \*\*\*Thiol\*\*\* Containing Esters and Cross-Linked \*\*\*Thiol\*\*\*  
 Containing Ester  
 DETD Particular aspects of the \*\*\*thiol\*\*\* containing esters,  
 hydroxy  
 \*\*\*thiol\*\*\* containing esters, cross-linked \*\*\*thiol\*\*\*  
 ester,  
 unsaturated esters and epoxidized unsaturated esters are measured  
 particular analytical techniques. \*\*\*Thiol\*\*\* sulfur values  
 were  
 obtained using a silver nitrate titration as described in ASTM  
 D3227 or  
 by Raman spectroscopy. Carbon-carbon double bond to \*\*\*thiol\*\*\*  
 group molar ratio, cyclic sulfide to \*\*\*thiol\*\*\* group molar  
 ratios  
 were determined by .sup.13C NMR and/or GC analysis of the  
 \*\*\*thiol\*\*\*  
 containing ester or hydroxy \*\*\*thiol\*\*\* containing ester side  
 chains.  
 DETD \*\*\*Thiol\*\*\* Sulfur Content by Raman Spectroscopy  
 DETD \*\*\*Thiol\*\*\* sulfur content was measured by both silver  
 nitrate  
 titration, ASTM D3227, and/or Raman spectroscopy. The Raman  
 spectroscopy  
 method is practiced by measuring the Raman spectra of the  
 \*\*\*thiol\*\*\*  
 containing ester, hydroxy \*\*\*thiol\*\*\* containing ester,  
 cross-linked  
 \*\*\*thiol\*\*\* ester and comparing the spectra to calibration

standards containing known compounds having known amounts of  
 groups. Generally, the calibration standard  
 compound has a similar structure to the  
 containing esters analyzed.  
 DETD The containing esters, hydroxy containing esters and cross-linked ester  
 content were determined by comparing the Raman spectra of the  
 containing esters, hydroxy  
 esters and cross-linked ester to calibration  
 standards prepared from mercaptanized methyl oleate diluted in soybean oil  
 to known sulfur contents. Sulfur calibration standards were prepared using standards using various  
 known concentration of mercaptanized methyl oleate diluted in soybean  
 oil.  
 DETD Raman spectra of the calibration standards and the containing esters, hydroxy containing esters and cross-linked ester were measured using a Kaiser  
 Hololab 5000 Process Raman spectrometer, using a 785 nm laser.  
 containing esters, hydroxy containing esters and cross-linked ester samples and the sulfur calibration standard Raman spectra were obtained by  
 collecting four 10 second scans which were then processed using Holoreact  
 software. Sulfur values for the containing esters, hydroxy containing esters and cross-linked ester were then calculated using the ratio of the peak area  
 values of the SH peak (center: 2575 cm<sup>-1</sup>; area 2500-2650 cm<sup>-1</sup>),  
 and the C=C peak (center--1745 cm<sup>-1</sup>; area--1700-1800 cm<sup>-1</sup>)  
 and comparing them to the peak area values for the calibration  
 standards and interpolating the containing esters, hydroxy  
 containing esters and cross-linked ester  
 sulfur contents. Repeatability of the sulfur values as measured  
 by Raman spectroscopy have been shown to have a standard  
 deviation of 0.05-0.1 and a % RSD of 0.6-1.5 using 5 samples having a %  
 sulfur content ranging from 3.1-10.6 weight percent as measured  
 over a two month period.  
 DETD The Raman spectroscopy technique for determining the

\*\*\*thiol\*\*\*  
 sulfur content of a \*\*\*thiol\*\*\* containing ester, hydroxy  
 \*\*\*thiol\*\*\* containing ester, and a cross-linked  
 \*\*\*thiol\*\*\*  
 containing ester has been illustrated using a \*\*\*thiol\*\*\*  
 containing  
 ester produced from soybean oil. However, one skilled in the art  
 may  
 adapt and apply the Raman spectroscopy technique for determining  
 the  
 \*\*\*thiol\*\*\* sulfur content of other \*\*\*thiol\*\*\*  
 containing esters,  
 hydroxy \*\*\*thiol\*\*\* containing esters, and a cross-linked  
 \*\*\*thiol\*\*\* containing esters described herein.  
 DETD C.dbd.C to \*\*\*Thiol\*\*\* Group and Cyclic Sulfide Group to  
 Tool Group  
 Molar Ratios by .sup.13C NMR  
 DETD Carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio  
 and  
 cyclic sulfide group to \*\*\*thiol\*\*\* group molar ratios were  
 determined by .sup.13C NMR. \*\*\*Thiol\*\*\* containing ester  
 .sup.13C  
 NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a  
 Varian  
 Mercury Plus 300 NMR, or equivalent spectrometer (75.5 MHz  
 .sup.13C  
 NMR). Peak areas were determined for the cyclic sulfide carbon  
 atoms,  
 \*\*\*thiol\*\*\* group HS--C carbon atoms and carbon-carbon double  
 bonds  
 carbon atoms using the .sup.13C NMR regions indicated in the  
 table  
 below:

Functional Group	.sup.13C NMR Region	Number of Carbon Atoms/Group
Cyclic Sulfide Carbon Atoms	49-49.5 ppm	2
HS--C Carbon Atoms	40-41.5 ppm	1
C.dbd.C Carbon Atoms	120-140 ppm	2
DETD The ***thiol***	containing ester cyclic sulfide to	
***thiol***	group molar ratio were calculated by dividing the cyclic sulfide	
carbon	atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon	
atoms per	cyclic sulfide group) and dividing the resultant number by the	
	***thiol*** group HS--C carbon atoms .sup.13C NMR peak area.	
The	***thiol*** containing ester carbon-carbon double bond to	
	***thiol*** group molar ratio were calculated by dividing the	
C.dbd.C	carbon atoms .sup.13C NMR peak area by 2 (to account for the 2	
carbon	atoms per carbon-carbon double bond) and dividing the result	
number by	the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak	
area	Offset sample .sup.13C NMR's for soybean oil and a ***thiol***	



containing ester produced from soybean oil using the disclosed process is provided as FIG. 1.

DETD The NMR technique for analyzing the unsaturated ester and the \*\*\*thiol\*\*\* containing ester produced from an unsaturated ester have been illustrated using .sup.13C NMR on soybean oil the \*\*\*thiol\*\*\* containing ester produced from soybean oil. However, one skilled in the art may adapt and apply either the .sup.13C NMR or .sup.1H NMR technique to analyze the unsaturated esters and \*\*\*thiol\*\*\* containing ester produced from the unsaturated ester described herein.

DETD \*\*\*Epoxide\*\*\* Group to \*\*\*Thiol\*\*\* Group Molar Ratios by .sup.13C or .sup.1H NMR

DETD The \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratios were determined using .sup.1H or .sup.13C NMR. Hydroxy \*\*\*thiol\*\*\* containing ester .sup.1H or .sup.13C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (300 MHz .sup.1H NMR-75.5 MHz .sup.13C NMR).

Peak areas were determined for the \*\*\*epoxide\*\*\* group and sulfide group using the .sup.13C and or .sup.1H regions indicated in the table below:

Functional Group	.sup.1H NMR Region	.sup.13C NMR Region	Number of Carbon Atoms/Group	Number of Hydrogen Atoms/Group
***Epoxide*** Group	2.75-3.2 ppm	53.6-56.6 ppm	2	
2 Carbon Atoms HS--C Carbon Atoms	3.2-4 ppm	40-41.5 ppm	1	1
DETD The hydroxy group to	***thiol***	containing ester	***epoxide***	
(to	***thiol***	group molar ratio were calculated by dividing the	***epoxide***	group carbon atoms .sup.1H NMR peak area by 2
group	account for the 2 hydrogen atoms attached to the	***epoxide***		
the	carbon atoms) and dividing the result number by the	***thiol***		
to	group HS--C carbon atom hydrogens 1C NMR peak area. Similarly,	hydroxy	***thiol***	containing ester
peak	***thiol***	group molar ratio were calculated using 13H NMR		
DETD	areas.	The average number of	***epoxide***	group per epoxidized
methods	unsaturated ester molecule can be determined utilizing similar			

utilizing either the carbonyl group carbon atom or the C--O ester group carbon atoms .sup.13C NMR peak areas in conjunction with the \*\*\*epoxide\*\*\* group .sup.13C NMR peak area. Sample .sup.1H NMR's epoxidized soybean oil and a \*\*\*thiol\*\*\* containing ester produced from epoxidized soybean oil 1 are provided in FIG. 2.

DETD The NMR technique for analyzing the epoxidized unsaturated ester and the \*\*\*thiol\*\*\* containing ester produced from an epoxidized unsaturated ester (a hydroxy \*\*\*thiol\*\*\* containing ester) has been illustrated using .sup.1H NMR on epoxidized soybean oil the \*\*\*thiol\*\*\* containing ester produced from epoxidized soybean oil.

However, one skilled in the art may adapt and apply either the .sup.1H NMR or .sup.13C NMR technique to analyze the epoxidized unsaturated esters and \*\*\*thiol\*\*\* containing ester produced from the epoxidized unsaturated ester described herein.

DETD Analysis of Unsaturated Esters, Epoxidized Unsaturated Esters, \*\*\*Thiol\*\*\* Containing Esters, and Hydroxy \*\*\*Thiol\*\*\* Containing Esters by Methanolysis

DETD Many properties of the unsaturated esters, epoxidized unsaturated esters, \*\*\*thiol\*\*\* containing esters, and hydroxy \*\*\*thiol\*\*\* containing ester were and/or can be determined by converting the complex ester molecules into their component polyols and carboxylic acid methyl esters. The converted esters are then analyzed by gas chromatography (GC) and/or gas chromatography/mass spectrometry (GCMS) to determine the composition of the complex ester side chains. Properties that are or can be determined by the methanolysis followed by GC or GC/MS of the carboxylic acid methyl esters include the number of side chain that contain \*\*\*thiol\*\*\* groups, the percent of \*\*\*thiol\*\*\* group sulfur, the number of (or average number) of double bonds per ester molecule, the molecular weight distribution (or average molecular weight) of the ester side chains, The number of (or average number of) \*\*\*epoxide\*\*\* groups per ester molecule, the cyclic sulfide to \*\*\*thiol\*\*\* group molar ratio, the carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio, and the \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio, among others.

DETD Depending upon the material being subjected to the methanolysis procedure, there are two methanolysis procedures that were

practiced upon the unsaturated ester, epoxidized esters, \*\*\*thiol\*\*\* containing ester, and hydroxy \*\*\*thiol\*\*\* containing esters described within the experimental section.

DETD Unsaturation esters and \*\*\*thiol\*\*\* containing ester produced from unsaturated ester were subjected to a hydrogen chloride based methanolysis procedure. In the hydrogen chloride methanolysis procedure, a 50 to 100 mg sample of the \*\*\*thiol\*\*\* containing ester is contacted with 3 mL of 3 N methanolic HCl and reacted for 2 hours

a 50.degree. C. The solution is then allowed to cool and the neutralized with a dilute sodium bicarbonate solution. The solution's organic components are then extracted with ethyl ether and analyzed by GC and/or GC/MS. Additional details for the methanolic hydrogen chloride methanolysis procedure may be found in the product specification sheet for methanolic HCl, 0.5 N and 3 N as supplied by Supelco.

DETD Epoxidized unsaturated esters and hydroxy \*\*\*thiol\*\*\* containing esters produced from epoxidized unsaturated esters were subjected to a sodium methoxide based methanolysis procedure. The sodium methoxide methanolysis procedure was based upon the procedure disclosed in U.S. Pat. No. 3,991,089. In the sodium methoxide methanolysis procedure, approximately 1 g of the ester was placed in a 50 mL vial with 5.0 mL 25% sodium methoxide in methanol, and 10 mL methanol. The mixture was shaken for approximately 1 hour at room temperature, during which time the solution became one phase. The mixture was then poured into 25 mL of distilled water. Diethyl ether, 25 mL, was added to the solution and the mixture was acidified with 0.5 N HCL to a pH of approximately 5. The organic layer was separated from the aqueous layer using a separatory funnel. The organic layer was washed successively with distilled water (15 mL) and brine solution (15 mL) and then dried over magnesium sulfate. The magnesium sulfate was separated from the organic solution by filtration and the solvent removed by rotary evaporation.

DETD FIG. 3 provides a GC/MS trace of a mercaptanized soybean oil subjected to the methanolysis procedure and analyzed by GC/MS using a HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 11 provides the GC/MS trace peak assignments.

TABLE 11

GC/MS Data for Methanolysis of A \*\*\*Thiol\*\*\* Containing Ester  
 Produced from  
 Soybean Oil  
 GC Retention time Methyl Ester Carboxylic Acid Assignment

21.58	Methyl hexadecanoate
23.66	Methyl (C18 monoene)oate
23.74	Methyl (C18 monoene)oate
23.96	Methyl octadecanoate
26.46	Methyl (C18 Monoene monomercaptan)oate
26.59	Methyl (C18 Monoene monomercaptan)oate
26.66	Methyl (C18 Monoene monomercaptan)oate
26.80	Methyl (C18 monomercaptan)oate
27.31	Methyl (C18 cyclic sulfide)oate
27.44	Methyl (C18 cyclic sulfide)oate
29.04	Methyl (C18 dimercaptan)oate
29.15	Methyl (C18 dimercaptan)oate
29.37	Methyl (C18 monoene dimercaptan)oate
29.46	Methyl (C18 monoene dimercaptan)oate
30.50	Methyl (C18 di (cyclic sulfide))oate

Peaks at 29.37 or 29.46 could also contain Methyl (C18 cyclic sulfide monomercaptan)oate isomers as part of those peaks.

DETD FIG. 5 provides a GC/MS trace of an epoxidized soybean oil contacted with hydrogen sulfide (a hydroxy \*\*\*thiol\*\*\* containing ester) subjected to the methanolysis procedure and analyzed by GC/MS using a HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 13 provides the GC/MS trace peak assignments.  
 TABLE 13

GC/MS Data for Methanolysis of a Hydroxy \*\*\*Thiol\*\*\* Containing Ester  
 Produced from Epoxidized Soybean Oil  
 GC  
 Retention time Methyl Ester Carboxylic Acid Assignment

16.09	Methyl hexadecanoate
17.68	Methyl octadecanoate
18.94	Methyl (C18 monoepoxide)oate
19.94	Methyl (C18 diepoxide)oate
20.14	Methyl (C18 diepoxide)oate
20.75	Methyl (C18 monohydroxy monothiol)oate
21-21.5	Methyl (C18 triepoxide)oate
22.82	Methyl (C18 dihydroxy dithiol)oate
22.90	Methyl (C18 monoepoxide monohydroxy monothiol)oate
27-27.5	Unidentified mixture of C18 sulfur containing methyl esters

DETD The methanolysis procedure and GC/MS procedure has been illustrate using soybean oil, epoxidized soybean oil, and the \*\*\*thiol\*\*\* containing products derived from soybean oil and epoxidized soybean oil.  
 However, one skilled in the art can easily adapt the procedures

to the analysis of other unsaturated esters, epoxidized unsaturated ester, and the \*\*\*thiol\*\*\* containing products derived from the unsaturated esters and epoxidized unsaturated esters as described herein.

DETD The polythiourethane produced from the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters, and cross linked \*\*\*thiol\*\*\* containing ester were analyzed using ASTM E1545-95A and E228-95 to provide the glass transition temperatures and the coefficients of thermal expansion. Shore hardness of the polythiourethanes were determined using ASTM D2240-02A. The polythiourethane were also subject to a subjective analysis classifying the polythiourethanes as hard, flexible, rubbery, rigid, tough, brittle, and other characteristics.

CLM What is claimed is:

1. A cross-linked \*\*\*thiol\*\*\* ester composition comprising \*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

CLM What is claimed is:

2. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 1, wherein the \*\*\*thiol\*\*\* ester oligomers have at least three \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

CLM What is claimed is:

3. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 1, wherein the \*\*\*thiol\*\*\* ester oligomers have from 3 to 20 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

CLM What is claimed is:

4. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 1, wherein the crosslinked \*\*\*thiol\*\*\* ester composition comprises \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers.

CLM What is claimed is:

5. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 4, wherein the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content from 0.5 to 8 weight percent.

CLM What is claimed is:

6. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 4, wherein the combined \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have an average molecular weight greater than 2000.

CLM What is claimed is:

7. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 4, wherein the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have an average molecular weight from 2000 to 20,000.

CLM What is claimed is:  
8. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 4, wherein the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total sulfur content ranging from 8 to 15 weight percent.

CLM What is claimed is:  
9. A cross-linked \*\*\*thiol\*\*\* ester composition produced by the process comprising the steps of: a) contacting a \*\*\*thiol\*\*\* ester composition with an oxidizing agent; and b) reacting the \*\*\*thiol\*\*\* ester and the oxidizing agent to form \*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

CLM What is claimed is:  
10. A process to produce a cross-linked \*\*\*thiol\*\*\* ester composition comprising: a) contacting a \*\*\*thiol\*\*\* ester composition with an oxidizing agent; and b) reacting the \*\*\*thiol\*\*\* ester and the oxidizing agent to form \*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

CLM What is claimed is:  
13. The process of claim 10, wherein the \*\*\*thiol\*\*\* ester is a hydroxy \*\*\*thiol\*\*\* ester.

CLM What is claimed is:  
14. The process of claim 10, wherein a weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester molecules ranges from 0.5 to 32.

CLM What is claimed is:  
15. The process of claim 10, wherein step of the reacting the \*\*\*thiol\*\*\* ester and the oxidizing agent is performed at a temperature ranging from 25.degree. C. to 150.degree. C.

CLM What is claimed is:  
16. The process of claim 10, wherein residual hydrogen sulfide is stripped from the cross-linked \*\*\*thiol\*\*\* ester composition produced.

CLM What is claimed is:  
 17. The process of claim 12, wherein the reaction of the  
 \*\*\*thiol\*\*\*  
 ester and the elemental sulfur is catalyzed.

IT 102-85-2, Tri-n-butylphosphite \*\*\*6674-22-2\*\*\* ,  
 1,8-Diazabicyclo[5.4.0]undec-7-ene  
 (activator; thiol ester comps. prepd. by reacting H2S with  
 unsatd. esters, such as soybean oil for manuf. monomers for prodn. of  
 polythiourethanes for fertilizers)

L7 ANSWER 49 OF 60 USPATFULL on STN  
 ACCESSION NUMBER: 1999:128662 USPATFULL <<LOGINID::20091205>>  
 TITLE: Reacting methylene and alkene components in  
 presence of tertiary amine reacted with \*\*\*epoxide\*\*\*  
 INVENTOR(S): Schindler, F. J., Fort Washington, PA, United  
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 (U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 5969046		19991019
APPLICATION INFO.:	US 1991-683126		19910409 (7)
RELATED APPLN. INFO.:	Continuation of Ser. No. US 1989-338433, filed on 13 Apr 1989, now abandoned which is a continuation of Ser. No. US 1986-952122, filed on 18 Nov 1986, now abandoned		
DOCUMENT TYPE:	Utility		
FILE SEGMENT:	Granted		
PRIMARY EXAMINER:	Sellers, Robert E.		
LEGAL REPRESENTATIVE:	Bakule, Patent Agent, Ronald D.		
NUMBER OF CLAIMS:	33		
EXEMPLARY CLAIM:	1		
LINE COUNT:	2014		
CAS INDEXING IS AVAILABLE FOR THIS PATENT.			
TI	Reacting methylene and alkene components in presence of tertiary amine reacted with ***epoxide***		
AB	A method for reacting a methylene-containing component such as an acrylic polymer prepared from acetoacetoxyalkyl (meth)acrylate and an alkene-containing component such as a polyfumarate, polymaleate, a polyester containing both fumarate and maleate groups or a polyacrylate comprises the reaction of a tertiary amine such as triethylene diamine and an ***epoxide*** such as a glycidyl-functional (meth)		

acrylic polymer in the presence of the methylene-containing component and alkene-containing component. The tertiary amine can be incorporated into the alkene-containing component such as the reaction of an unsaturated polyester with a compound having both tertiary amine and primary or secondary amine groups. The tertiary amine can be incorporated into the methylene-containing component such as an acrylic polymer derived from a tertiary amino-functional monomer and acetoacetoxyalkyl (meth)acrylate.

The \*\*\*epoxide\*\*\* can be incorporated into the methylene-containing component such as an acrylic polymer obtained from glycidyl (meth)acrylate and acetoacetoxyalkyl (meth)acrylate. The \*\*\*epoxide\*\*\* can be incorporated into the alkene-containing component.

SUMM This invention relates to ambient cure compositions based on the base-activated Carbon Michael reaction between active methylene groups and active alkene groups. More particularly, the invention is directed toward use of tertiary amines and \*\*\*epoxides\*\*\* to activate the Carbon Michael reaction. In more specific aspects, the invention is directed toward classes of active methylene groups, active alkene groups, tertiary amines and \*\*\*epoxides\*\*\* that provide low cost, color and hazard, in two-pack coatings with good pot life, cure speed, gloss and durability on exposure to high humidity and ultraviolet light. Two-pack aliphatic urethane coatings represent the best current technology and provide targets for pot life, cure speed, gloss and durability, but alternatives to urethanes are needed with advantages in economy, safety, and ease of handling, especially for coatings with low levels of volatile solvent.

SUMM It has been discovered that the pot-life/cure, cure rate/gloss and packaging problems with preferred alkene-containing and methylene-containing components can be overcome by use of tertiary amines and \*\*\*epoxides\*\*\* as the main activator of Carbon Michael cure, with a key element being the occurrence of most of the reaction between tertiary amine and \*\*\*epoxide\*\*\* in the presence of both the activated alkene component and the activated methylene component. Without limiting the scope of the invention, it is believed that the activation of Carbon Michael cure results from the conversion of



the tertiary amine to a quaternized nitrogen compound via reaction with the epoxy group in the presence of the Michael-reactive components.

When tertiary amines are mixed with \*\*\*epoxides\*\*\* in the absence of Michael-reactive components the typical result is a complex mixture of quaternary ammonium compounds, their alkaline decomposition products, and polyether moieties from epoxy homopolymerization. It is believed that in the presence of activated methylene component the reaction between amine and \*\*\*epoxide\*\*\* forms quaternary ammonium salts with the weakly acidic methylene component, activating the methylene component for reaction with the alkene component.

SUMM Without limiting the scope of the invention, the pot-life/cure problem is believed overcome by two fundamental advantages of this method of activation. First, the pot-life is extended because the activator concentration starts at a low level, and second, the rate of formation of activator is greater in the film than in the pot because the concentrations of amine and \*\*\*epoxide\*\*\* increase due to loss of solvent.

SUMM Without limiting the scope of the invention, the cure-rate/gloss problem is believed overcome by the same mechanism as the pot-life/cure problem. The cure rate increases with time as activator is formed from reaction of amine and \*\*\*epoxide\*\*\*, allowing solvent to leave the film while it is thermoplastic, yet giving a fast cure as sufficient levels of activator are formed.

SUMM Triethylenediamine does not give sufficient activation of Carbon Michael cure in the absence of \*\*\*epoxide\*\*\*. However, in the presence of \*\*\*epoxide\*\*\*, triethylenediamine gives faster activation than other tertiary amines, which is useful when a fast cure rate is needed.

SUMM When both the tertiary amine component and the \*\*\*epoxide\*\*\* component are low in molecular weight and not selected according to the preferred embodiments described below, films prepared using the invention tend to blister when exposed to water. This problem is overcome by a variety of solutions involving either the amine component or the \*\*\*epoxide\*\*\* component:(1) the amine can be

incorporated into the active methylene component, for example by use of acrylic copolymers that contain both pendant acetoacetate moieties and tertiary amine from amine-containing monomers such as dimethylaminoethyl methacrylate or dimethylaminopropyl methacrylamide; (2) the amine can be incorporated into the alkene component; (3) the \*\*\*epoxide\*\*\* can be incorporated into the active methylene component, for example by use of acrylic copolymers that contain both pendant acetoacetate moieties and \*\*\*epoxide\*\*\* from copolymerization of glycidyl methacrylate, or (4) the \*\*\*epoxide\*\*\* can be incorporated into the alkene component.

SUMM A preferred class of amine-containing active methylene components is derived from copolymerization of a monomer mixture containing both acetoacetate-functional and tertiary amine-functional monomers such as dimethylaminoethyl methacrylate or dimethylaminopropyl methacrylamide. The level of the tertiary amine-functional monomer is selected according to the level of the acrylic polymer in the binder, to provide, along with other amine components, the ratios of amine to \*\*\*epoxide\*\*\* specified below. The level of tertiary amine-functional monomer then is from about 2 percent by weight of total monomer for binders with a high level of acrylic to 15 percent for binders with a low level of acrylic.

SUMM The preferred \*\*\*epoxide\*\*\* components contain the \*\*\*epoxide\*\*\* group as glycidyl esters, glycidyl ethers, or epoxidation products of alpha olefins. A preferred type for economy is the commercial liquid diglycidyl ether of bisphenol A, for example EPON 828 from Shell. Other types of \*\*\*epoxide\*\*\* give slower cure, presumably because of their slower reaction rate with tertiary amines. For best water resistance, especially with low molecular weight amine components, the \*\*\*epoxide\*\*\* is incorporated in the Michael-reactive methylene or alkene component, for example by use of glycidyl methacrylate to give glycidyl esters in an acrylic copolymer containing pendant active methylene moieties. However, for economy and ease of adjustment of

\*\*\*epoxide\*\*\* level, one can use low molecular weight glycidyl esters, glycidyl ethers, or epoxidation products of alpha olefins. When using the low molecular weight \*\*\*epoxide\*\*\* components, for best water resistance it is preferred to use an amine component incorporated into the Michael-reactive methylene or alkene component, or capable of reaction with one of the Michael-reactive components during cure.

SUMM A preferred method for incorporation of the \*\*\*epoxide\*\*\* in the Michael-reactive methylene component is use of acrylic polymers containing pendant acetoacetate groups, incorporating \*\*\*epoxide\*\*\* by use of a monomer mixture containing glycidyl methacrylate along with acetoacetate-functional monomer. The level of glycidyl methacrylate in the acrylic polymer is selected according to the level of acrylic polymer in the binder, the level of any other acrylic or \*\*\*epoxide\*\*\* components, and the criteria for total \*\*\*epoxide\*\*\* level discussed below. With a high level of acrylic polymer and all of the acrylic polymer containing \*\*\*epoxide\*\*\*, the glycidyl functional monomer may be as low as 4 percent in the acrylic polymer. When both an amine-functional acrylic and an epoxy-functional acrylic are used, the preferred level of glycidyl methacrylate may be 20 percent or more of the acrylic polymer with glycidyl and acetoacetate functionality.

SUMM There are three preferred ways to combine Carbon Michael-reactive, \*\*\*epoxide\*\*\*, and amine components to achieve stable packages. The \*\*\*epoxide\*\*\* can be mixed prior to use with the active methylene moieties, the Carbon Michael-reactive alkene moieties, or a combination of the Michael-reactive components.

SUMM A particularly preferred method for achieving two packages of similar size is combination of the \*\*\*epoxide\*\*\* with either the active methylene moieties or the alkene moieties, and the tertiary amine with the other Carbon Michael-reactive component.

SUMM The ratio of total moles of tertiary amine groups to \*\*\*epoxide\*\*\* groups is not critical, but is usually from about 0.5 to about 1.5. Since the speed of cure increases with concentration of both amine and

is           \*\*\*epoxide\*\*\* groups, and the presence of an excess of amine detrimental to acid resistance and weathering resistance, it is preferred to have the ratio of tertiary amine groups to \*\*\*epoxide\*\*\* groups from about 0.5 to about 1.0.

SUMM A useful statistic for the activator level is milliequivalents of \*\*\*epoxide\*\*\* per 100 grams of all activator and Carbon Michael reactive components, based on non-volatile material. This gives a measure of the potential moles of strong base per total weight of binder. This number should exceed the level of acid in the binder by at least 2 milliequivalents/100 grams. When the binder contains low levels of acid, the preferred activator level is usually in the range 2-80 milliequivalents per 100 grams, and often in the range 10-40, with lower levels giving poor rate of cure and higher levels giving adverse effects on water or acid resistance.

SUMM The \*\*\*epoxide\*\*\* /tertiary amine activator can be supplemented by less than about 10 milliequivalents of preformed strong base per hundred grams of binder, with the strong base selected from the group consisting of salts of tetramethylguanidine, 1,8-diazabicyclo(5.4.0)undec-7-ene, or quaternary ammonium hydroxide with carbonic, acetic or hydrofluoric acids and mixtures thereof to accelerate cure. The level of strong base should be kept to the minimum level giving the desired improvement in early cure, due to adverse effects on water resistance. The carbonic salts give the best improvement of early surface cure, and are therefore usually preferred. This is thought to be due to the ease of loss of acid from the film as carbon dioxide. However, even at 10 milliequivalents per hundred grams of binder, the carbonic salts tend to give loss of gloss, and thick films can even wrinkle due to surface cure exceeding sub-surface cure and solvent loss.

SUMM Improvement of early cure without the problems of preformed base can be accomplished by use of phenols, or combinations of phenols and alcohols. Without limiting the scope of the invention, it is believed that phenols and alcohols accelerate the reaction between tertiary amines and \*\*\*epoxides\*\*\*. Preferred phenols are alkylsubstituted, for

example  
p(t-butyl)phenol and nonylphenol. Preferred levels of phenol are  
about 5 to about 30 milliequivalents per 100 grams total weight of  
activator plus Carbon Michael-reactive components. The alcohols are used at  
from 1 to 20 percent of the binder, with a preferred alcohol being  
2-ethylhexanol.

SUMM With hydroxyl-terminated polyesters, hardness and chemical  
resistance can be improved by adding multifunctional isocyanate at the time  
of mixing Carbon Michael-reactive components, tertiary amine and  
\*\*\*epoxide\*\*\* .

SUMM The invention also relates to coating or binder compositions  
including active methylene moieties, Michael-reactive alkene groups,  
\*\*\*epoxide\*\*\* groups, tertiary amines and supplementary  
additives for improvement of early cure.

DETD Three hundred twenty (320) grams of reagent grade xylene solvent  
was weighed into a one liter four neck flask. A monomer mix was  
prepared from 96 grams methyl methacrylate, 96 grams butyl methacrylate,  
96 grams styrene, 192 grams AAEM, and 7.2 grams of t-butyl peroctoate. A  
solution of n-dodecyl \*\*\*mercaptan\*\*\* was prepared by dissolving 12.1  
grams of the \*\*\*mercaptan\*\*\* in enough of the solvent to make 60 ml  
of solution. The remaining solvent was stirred with a nitrogen  
sparge and heated to 105 degrees C. The monomer mix and \*\*\*mercaptan\*\*\*  
solution were then added simultaneously over a period of 95  
minutes at 103-106 degrees C. Following completion of the additions the  
mixture was held at 105 degrees C. for another 150 minutes with 2 gram  
portions of t-butyl peroctoate being added after 45 and 95 minutes. The  
resulting 816 grams of solution was found to contain 60.9 wt. % polymer  
solids. Gel permeation chromatography indicated that the molecular  
weights were Mw=15,200, Mn=5560. The monomer ratio was 40 AAEM/20 MMA/20  
BMA/20 Styrene. The initiator was 1.5% t-butyl peroctoate on polymer  
solids. The chain regulator was 2.5% n-dodecyl \*\*\*mercaptan\*\*\* on  
polymer solids.  
DETD Polymer B was prepared by the same procedure used with Polymer A,  
except

for use of 1.5% 2,2'-azobis(2-methylbutanenitrile) as the initiator in place of t-butyl peroctoate, and use of 5.0% n-dodecyl \*\*\*mercaptan\*\*\* in place of 2.5%. Gel permeation chromatography indicated that the molecular weights were  $M_w=8170$ ,  $M_n=2720$ . DETD AAEM copolymers were prepared as described above except no \*\*\*mercaptan\*\*\* was used, the initiator was 2.16 wt. % t-butyl peroctoate on monomers, and the monomer compositions were as follows:

TABLE 3

Hardness development with only epoxy/amine latent catalyst.

		Knoop Hardness		
Epoxy Identification		14		
		Chemical Composition		
		1 day	8 day	day
<hr/>				
Araldite RD-1				
		Butyl Glycidyl Ether		
		0.32	0.69	0.82
Araldite CY-179				
		Cycloaliphatic Diepoxide		
		0.38	0.52	0.59
Araldite DY-025				
		C-12/C-14 Alkyl Glycidyl Ether		
		tacky	5.77	9.90
Araldite DY-027				
		C-8/C-10 Alkyl Glycidyl Ether		
		0.36	3.28	7.06
Araldite MY-720				
		N-Tetraglycidylmethylenbis-		
		0.34	1.54	5.72
Araldite Resin				
		4-Glycidyloxy-N,N-di-Glycidyl		
500		0.32	5.20	9.65
Araldite Resin				
		aniline		
510		0.38	4.54	9.72
Heloxyl MK-116				
		2-Ethylhexyl Diglycidyl Ether		
		0.36	4.38	9.24
Heloxyl WC-67				
		1,4- ***Butanediol*** Diglycidyl Ether		
		0.32	9.54	12.55
Heloxyl WC-68				
		Neopentylglycol Diglycidyl		
		0.33	9.18	11.85
Heloxyl MK-107				
		Ether		
		Cyclohexyldimethanol Diglyc.		
		0.32	8.86	12.35
Heloxyl WC-69				
		Ether		

	Resorcinol Diglycidyl Ether			
		0.31	9.80	13.00
Heloxyl WC-84	Aliphatic Polyol Di/Triglyc.			
	tacky	2.88	5.97	
	Ether			
Epon 828	Bisphenol A Diglycidyl Ether			
		0.39	9.82	14.40

DETD

TABLE 4

— Evaluation of TEDA and DMAM as tertiary amine for latent catalyst system with \*\*\*epoxides\*\*\* .

Amine	Epoxy	Gel 500 g Knoop Pencil	Butyl
Level	Level		
	Time		
	Zapon Hardness		
	Hardness		
	Acetate		
Amine (meq/100 grams)			
(Hrs)			
	(Minutes)		
	1 day		
	14 day		
	14 day		
	Patch		

— Enamels using AAEM copolymer without copolymerized amine.

DMAM	21	21	>120		
			344-382		
			0.36		
			9.97		
			F		<6B
DMAM	42	42	>120		
			514-1419		
			0.76		
			15.50		
			H		<6B
DMAM	63	63	98-120		
			521-1416		
			1.76		
			13.95		
			H		HB
DMAM	42	84	98-120		
			518-1409		
			1.20		
			13.1		
			H		HB
DMAM	42	126	76-98		
			514-1405		
			1.52		
			12.35		
			H		HB
DMAM	21	63	>120		
			511-1406		
			0.58		

				11.10		
				F	<6B	
TEDA	21	21	10-24			
			180-274			
			3.72			
			13.33			
			F	No Film		
TEDA	42	42	<5 172-270			
			5.52			
			12.75			
			F	<6B		
TEDA	63	63	<5 173-267			
			6.74			
			12.65			
			H	B		
TEDA	42	84	<5 312-348			
			3.49			
			13.27			
			H	<6B		
TEDA	42	126	<5 161-266			
			2.06			
			7.95			
			F	<6B		
TEDA	21	63	<5 408-456			
			1.99			
			8.36			
			F	<6B		

Enamel using AAEM copolymer with copolymerized amine.  
DMPMA

	21	21	>120			
			404-452			
			0.33			
			11.43			
			H	<6B		

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DETD The AAEM copolymers were prepared without \*\*\*mercaptan\*\*\* chain transfer agent, with the following monomer compositions and molecular weights (Mw/Mn) indicated by gel permeation chromatography:

DETD TABLE 6

Blue paint comparison of activation by tetrabutylammonium bicarbonate and by \*\*\*epoxide\*\*\* /tertiary amine with polyester as alkene component.

AAEM Copolymer	F/G (1/1) H	
Additive	TEDA	TBACARB
Blueness	Deep	Pale
Knoop Hardness at 1 day		
	1.6	1.3
Knoop Hardness at 4 days		
	4.5	1.5
Knoop Hardness at 14 days		
	8.9	2.4
Pencil Hardness at 1/4/14 days		
	B/F/H	B/B/B
Swell ratio at 4/14 days		



1.73/1.55 2.04/2.00  
 Direct Impact (in-lb) at 14 days  
                               70-90       50-70  
 20 degree gloss at 14 days  
                               81.2       66.0

DETD

TABLE 7

Blue paint comparison of activation by tetrabutylammonium bicarbonate and by \*\*\*epoxide\*\*\* /tertiary amine with TMPAOPA as alkene component.

AAEM Copolymer Additive	F/G (1/1)	H
Blueness	TEDA	TBACARB
	Nearly Deep	Pale
Knoop Hardness at 1 day		
	4.1	1.3
" 4 days	7.2	1.8
" 14 days	10.0	2.7
Pencil Hardness at 1/4/14 days		
	F/F/H	F/HB/HB
Swell ratio at 4/14 days		
	1.41/1.34	1.58/1.54
Direct Impact (in-lb) at 14 days		
	70-90	>130
20 degree gloss at 14 days		
	82.9	79.1

DETD Direct Comparison of Epoxy/Amine and Preformed Strong Base Activators

Using the Same AAEM Copolymer with Both Activators, and Demonstration of Advantages in Water Resistance with TEDA when the Epoxy Component is an

AAEM/GMA Copolymer Rather than a Low Molecular Weight

\*\*\*Epoxide\*\*\*

DETD Pigment dispersions were prepared with titanium dioxide as sole pigment,

using a sand grind procedure with AAEM copolymers as vehicle. The

AAEM

copolymers were prepared without \*\*\*mercaptan\*\*\*, using t-butyl

peroctoate as initiator with 4.5 or 9.0 weight percent t-butyl peroctoate based on monomers. The monomer composition was 40

AAEM/52

i-BMA/8 GMA. AAEM copolymer L, prepared with 9.0 percent t-butyl peroctoate, had Mw=9,960, Mn=2760. AAEM copolymer M, prepared

with 4.5 percent t-butyl peroctoate, had Mw=20,700, Mn=6910.

DETD White paints were prepared as described in Example 25, using AAEM Copolymer N and either TMPAOPATE or the repeat of Polyester C described

in Example 25. The binder composition for each paint contained a total

of 9.15 grams AAEM copolymer plus alkene component (TMPAOPATE or Polyester C). The remainder was 0.6 grams Epon 828 and 0.25 grams bis-DMAPA. All paints also contained 0.2 grams p-t-butyl phenol

and 0.01  
grams Silicone SF-1023, with xylene as solvent. AAEM copolymer N  
was  
prepared with monomer composition 40 AAEM/55 i-BMA/5 Styrene, 1  
weight  
percent 2,2'-azobis(2-methylbutanenitrile as initiator and 1% n-  
dodecyl  
\*\*\*mercaptan\*\*\*, and had Mw/Mn=21,900/9220.

CLM What is claimed is:  
1. A method for reacting a methylene-containing component and an  
alkene-containing component comprising mixing and reacting a  
tertiary  
amine and an \*\*\*epoxide\*\*\* in the presence of the  
methylene-containing component and the alkene-containing  
component  
wherein the tertiary amine is selected from the group consisting  
of a  
tertiary amino-functional acrylic polymer; a tertiary amino-  
functional  
polyester; triethylenediamine; a compound containing both  
tertiary amine  
and primary or secondary amine; a Mannich reaction product of a  
secondary amine, formaldehyde and a phenol; and mixtures thereof.

CLM What is claimed is:  
11. The method according to claim 1 wherein the \*\*\*epoxide\*\*\*  
is  
selected from the group consisting of a mono- and poly-functional  
glycidyl compound, a polyepoxide derived from an alpha-olefin and  
mixtures thereof.

CLM What is claimed is:  
18. The method according to claim 1 wherein the \*\*\*epoxide\*\*\*  
is a  
glycidyl-functional acrylic polymer and the tertiary amine is  
triethylenediamine.

CLM What is claimed is:  
19. The method according to claim 1 wherein the \*\*\*epoxide\*\*\*  
is  
selected from the group consisting of a mono-, di- and tri-  
functional  
glycidyl compound and a polyepoxide of an alpha olefin, and the  
tertiary  
amine is selected from the group consisting of a tertiary  
amino-functional acrylic polymer, a tertiary amino-functional  
polyester,  
a compound having both a tertiary amine and a primary or  
secondary  
amine, and mixtures thereof.

IT 62-49-7 \*\*\*280-57-9\*\*\*, 1,4-Diazabicyclo[2.2.2]octane 2052-  
49-5, Tetrabutylammonium hydroxide 17351-62-1  
(catalysts, coatings of methylene polymers, alkene polymers, and  
epoxides contg., for fast curing)

=>

---Logging off of STN---

=>

Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

85.61

103.37

STN INTERNATIONAL LOGOFF AT 14:33:00 ON 05 DEC 2009